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Use of Argon in the Ionization Method of Measuring Cosmic Rays and Gamma-Rays

JOHN J. HOPFIELD, *Basic Science Division, A Century of Progress*
(Received February 4, 1933)

The saturation-voltage, current characteristics of argon were studied at two pressures of argon and at four widely different ionization intensities produced by gamma-rays. Pressure-ionization curves for argon and for air were made. A comparison of the argon curve with the nitrogen one shows that argon is about twice as sensitive for use in ionization chambers for studying gamma-rays and cosmic rays. Some transient ionization effects are described. A comparison of the intensity of cosmic rays to gamma-rays was made and this ratio was found to be lower for argon than for air in the ionization chamber at the same pressure.

I. INTRODUCTION

THIS paper is chiefly concerned with the study of argon[1, 2] with reference to its ionization at high pressure by cosmic rays and by gamma-rays from radium. Since argon was to be used by Compton in an extensive geographical survey of cosmic rays, it was important to know its behavior with reference to the above rays. Some rather striking results were obtained with this gas; results that show its superiority over the gases air and nitrogen that had already been used by various investigators of cosmic radiation.

Some of the earliest work on the ionization of gases at high pressures was done by Erikson,[3] who investigated air to a pressure of 400 atmospheres, and carbon dioxide to the pressure of liquefaction. Unfortunately my present data on air are comparable with his only for the stronger currents. I deduce from his paper that the ionization he used was about 8 times the greatest used by me. His data were carried over a much wider range of pressures and potential gradients than any here recorded. Indeed from his work one can predict the ultimate form of the present curves and it is interesting to note to what extent these forms are developed.

Some of the results of Erikson are: (1) The saturation curves for air rise steeply for the first 50 volts and then swing over and continue to rise gradually for the rest of their course, never becoming horizontal, however, even at gradients of more than 1000 volts per cm. (2) The ionization-pressure curves for air reach flat maxima and descend with increasing pressure even in the case of the greatest potential gradient.

Some recent work of Bowen[4] on the ionization of air by gamma-rays carried over about the same range of pressure as the present work is valuable for comparison with the present data.

II. SATURATION CURVES FOR AIR AND FOR ARGON AT HIGH PRESSURES

The saturation data for argon were obtained in the following manner: The radium sample,

[1] A. H. Compton and J. J. Hopfield, Phys. Rev. **41**, 593L (1932).
[2] J. J. Hopfield, Phys. Rev. **41**, 904A (1932).
[3] H. A. Erikson, Phys. Rev. **27**, 473 (1908).
[4] I. S. Bowen, Phys. Rev. **41**, 24 (1932).

containing 0.971 mg of radium surrounded by a centimeter of lead, was placed at various distances from the center of a spherical bomb, 10 cm in diameter, which was the ionization chamber.[5] The bomb was made of steel and served as one electrode of the ionization chamber and a central wire connected to the needle of a Lindemann electrometer served as the other electrode. The "saturation" curves were made with voltages ranging from 4 to 200 volts applied between needle and bomb. This voltage was read from a high-resistance voltmeter and the ionization current was read from the electrometer. The constants of the apparatus were measured in order to reduce this current to ions per cc per sec.

The curves are shown at four ionization intensities (namely, with the radium at 30 cm, 1 m, 3 m, and infinity from the center of the bomb) for each of the two pressures (see Figs. 1, 2, 3, 4). Some of the more obvious things that are shown by these curves may be noted. Curves 1A, 1B, and 2A are far from saturation values even at the highest voltages used. This has already been shown by Erikson[3] for saturation curves in air. Curve 2B also has an upward trend. On the other hand the data of curves 3B and 4A, B show much less upward trend indicating that saturation was more nearly attained.

The data taken at the higher current intensities (Figs. 1 and 2) are much smoother than the data for smaller intensities (Figs. 3 and 4). This is perhaps due to the probability fluctuations of the weak radiation used for the latter data, and to fluctuations in the potential of the bomb due to faulty contacts, etc., which cause a corresponding induced potential on the electrometer. This source of error is more effective for the higher sensitivity of the electrometer used with the smaller currents.

The saturation curve for air 2C is much more nearly horizontal than 2B. This shows that it is easier to produce this form of saturation in air than in argon at about the same pressure.

Fig. 5 shows that any two of the above curves are not convertible into one another by a constant factor. This indicates quantitatively that the percentage of saturation at a given applied voltage is not constant with changing intensity of ionization but is a function of that intensity. This is at variance with some of the data of Bowen[4] taken in air. It is seen that the two smallest currents are nearest to coincidence. The other two show no semblance of coincidence. In Bowen's case the superposition of curves was good for large potential gradients and not so good for smaller ones. These data would correspond to his test with smaller gradients (see paragraph on potential distribution in the ionization chamber) and hence are to be compared only in such cases.

To account for the general shape of the curves and for their behavior when compared with one another one can picture the physical process to be the following: the gas in the bomb is traversed by many thin, nearly parallel tracks of intense ionization due to secondary swift electrons ejected by the gamma-rays. A few of the ions are pulled away from these tracks by the applied electric field and commingle in the bomb while they drift toward the electrodes. Recombination takes place in both the region of the parent tracks and in the intervening region. However, with a given distribution of potential gradient, the percentage of the ions lost by recombination in the parent tracks (since the tracks are too far apart to influence one another) is constant, i.e., independent of the number of tracks, or what amounts to the same thing, of the intensity of ionization. The ionization current, which is due to the ions outside the tracks, would then be proportional to the number of tracks and any two of the above curves should be exactly *superposable* by a constant factor. The fact that they are not, but drop lower for the higher intensities indicates that ions are lost by recombination in the interspaces, and moreover, the number thus lost (proportional decrease in current) is not proportional to the number of tracks but to some higher power or function of that number. The ordinary n^2 relation for recombination is expected to hold in this region.

This result, as already mentioned, seems to be at variance with the work of Bowen, who, however, experimented with small ionization

[5] A complete description of the apparatus will be published shortly in the Review of Scientific Instruments. See also A. H. Compton, Phys. Rev. **43**, 387 (1933).

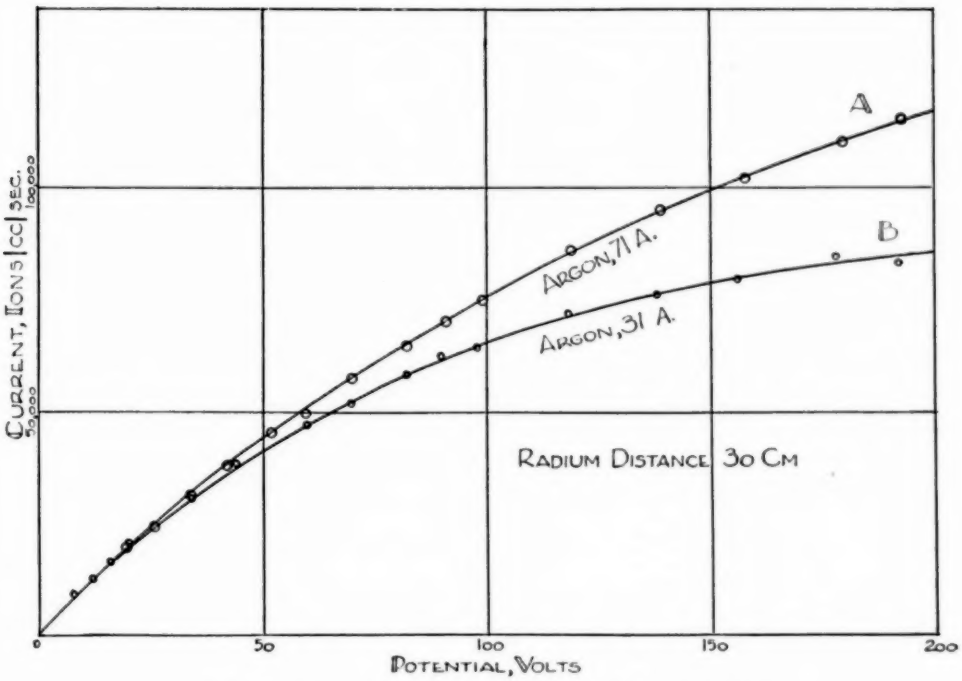

FIG. 1. Saturation current in argon, radium distance 30 cm.

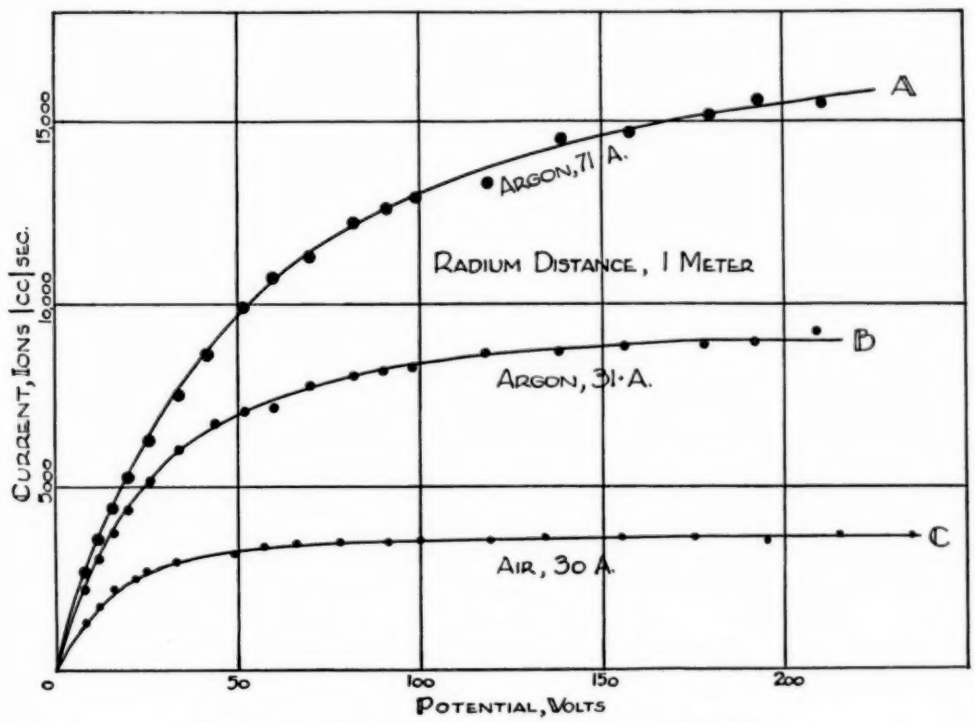

FIG. 2. Saturation current in argon and air, radium at 1 m.

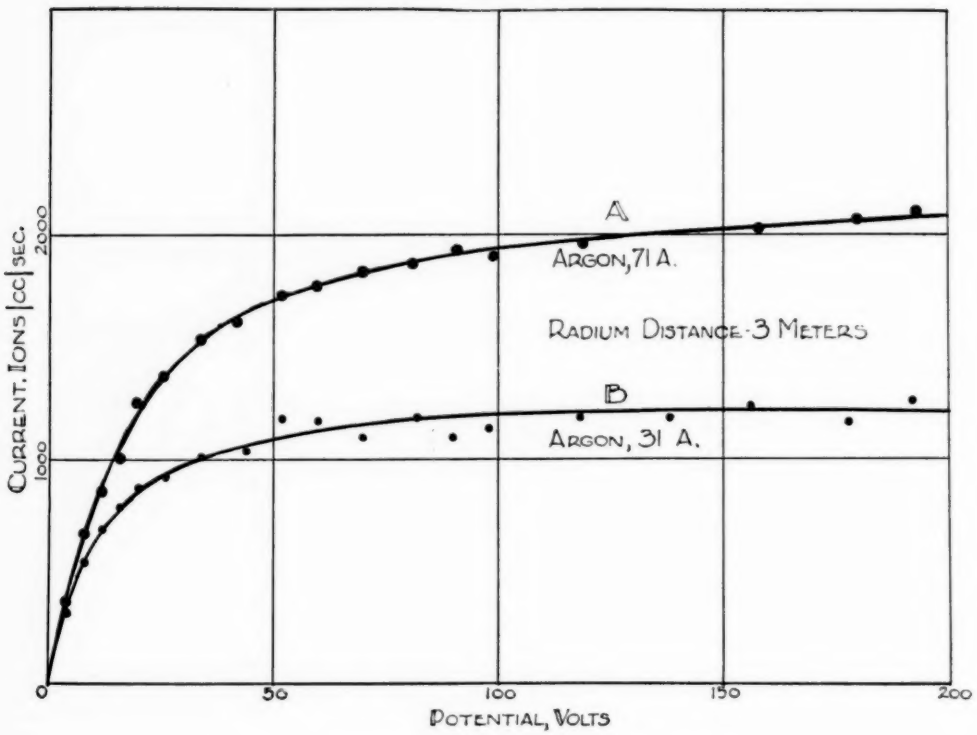

FIG. 3. Saturation current in argon, radium at 3 m.

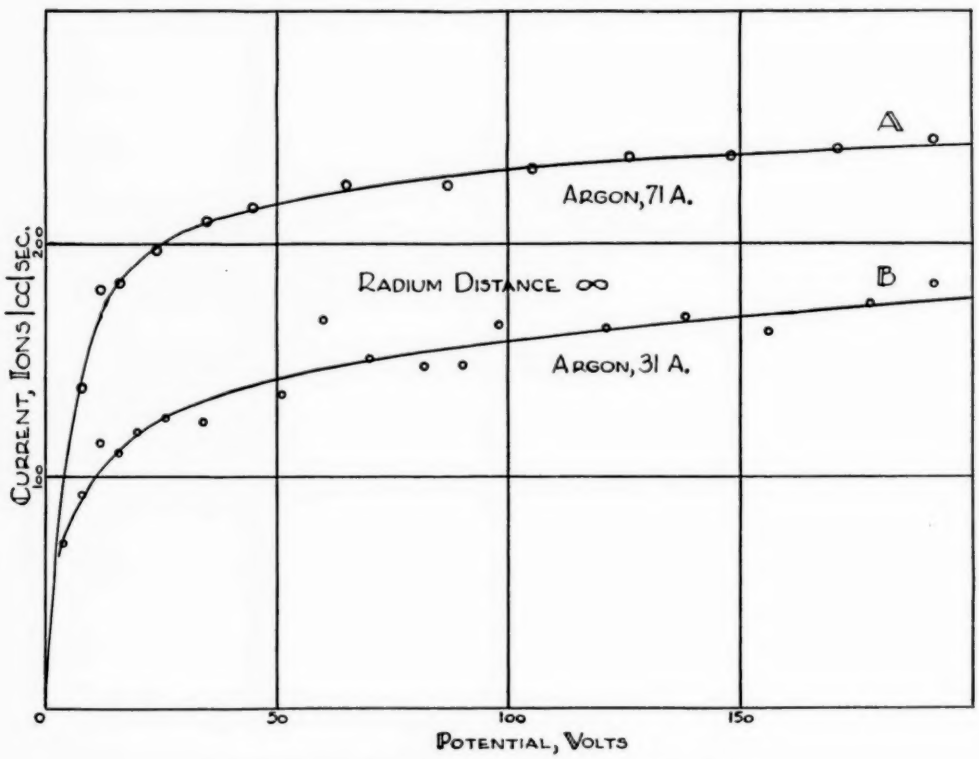

FIG. 4. Saturation current in argon, radium at infinity.

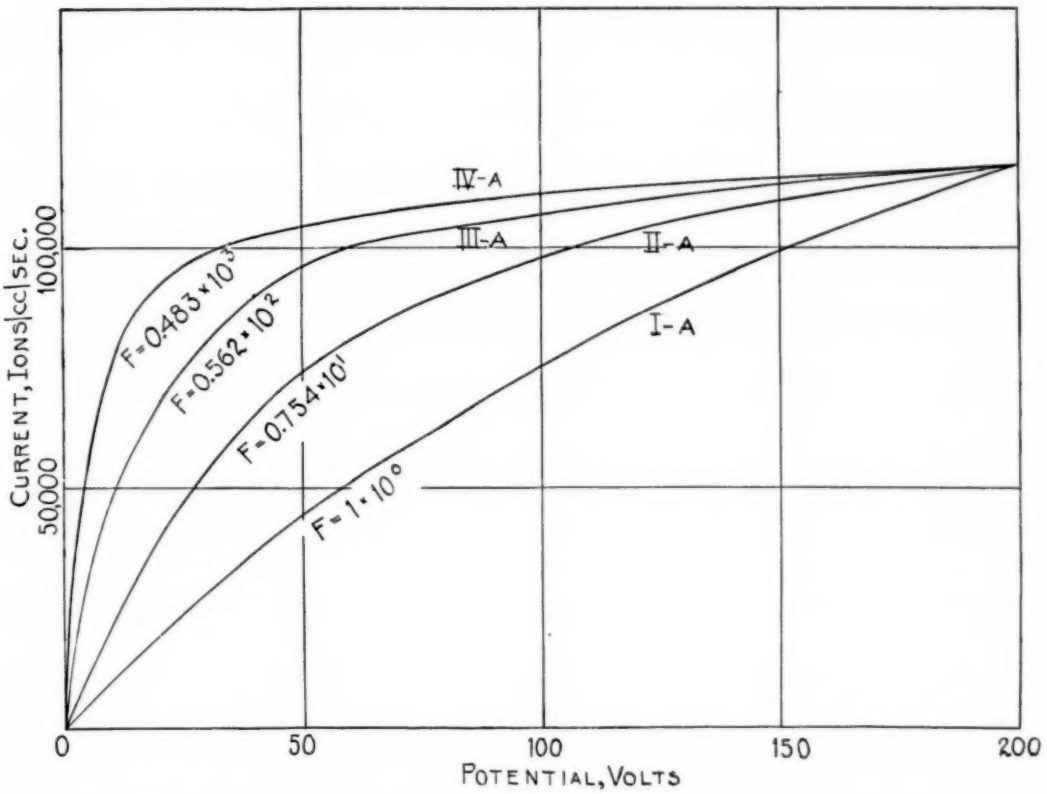

FIG. 5. Argon at 71 atm. Figs. 1–4 reduced to a common scale.

intensities. Also it does not agree with the conclusion of Compton[6] and others that recombination takes place only in the tracks of ionization.

The fact of columnar ionization lends itself well to explaining qualitatively the form of the ionization curves at different intensities as well as to pointing out some of the characteristics of the I–P curves discussed in a subsequent paragraph. The saturation curve at high pressure can be considered as formed by adding two ideal curves, the one rising rapidly with the voltage and bending over sharply to the horizontal at the saturation value even at comparatively low voltage, and the other starting from the origin and rising slowly with the slope of the actual ionization curve at high field intensities. The resultant curve would be the sum of these. The first part of the experimental curve (showing the rapid rise at low voltage) is chiefly due to the loose ions in the interspaces; the slowly rising second part is due to ions pulled from the tracks.

The design of the ionization chamber affects the distribution of the applied potential. By making the following simplifying assumptions: (a) that the central wire is very thin in comparison with the radius of the sphere; (b) that the charge is distributed uniformly over the surface of the sphere; (c) that the linear density of the charge on the wire is constant, it can be shown that the distribution of potential in the equatorial plane of the bomb normal to the central electrode has the following approximate values: the drop in potential for the outside centimeter of distance is 6 volts, if 144 volts is applied to the chambers; over the next centimeter 8.7 volts; the third centimeter 13.3; the fourth 24.0 and over the last centimeter 92 volts. The calculation shows that most of the potential drop occurs in a small volume near the center of the bomb and that the remainder of the volume of the bomb has a small potential gradient.

[6] A. H. Compton, R. D. Bennett and J. C. Stearns, Phys. Rev. **39**, 873 (1932).

III. Ionization-Pressure Curves for Air and for Argon

The ionization-pressure data for air and for argon were taken in the following manner: The bomb of the apparatus was pumped out well and then filled with air or with argon to the highest pressure. The gas was allowed to stand unused for about a day after filling. When ionization current readings were taken, the radium was at a distance of 100 cm from the center of the sphere, and the sphere was unshielded. A potential of 144 volts was placed on the sphere and the needle of the electrometer was at first connected to earth, the grounding key opened to allow the charge to accumulate on the needle, and the ionization current was read. The temperature of the gas was taken from a thermometer placed against the bomb. The pressures were read from a gauge connected to the bomb. The readings of current were taken first with +144 volts on the sphere and then with −144 volts on it, in order to reduce the effects of small electrical leaks. Some gas was then allowed to leak out slowly, the cock shut off, and after waiting an hour or more, readings were taken at the new pressure. The range of pressure covered for air was from 105 to 1 atmospheres, and for argon from 95 to 1 atmospheres. These data are plotted in Fig. 6, curves A and B. Curve C for nitrogen was taken from the work on ionization of nitrogen by Broxon.[7]

In explaining the form of these curves, Broxon[8] using simple assumptions and an ingenious analysis showed that the I–P curve for air fits a cubic equation in which the parameters are all determined from the data. However, his theory[9] yielded an absorption coefficient for cosmic rays which he concedes is too large. Compton, Bennett and Stearns, on the other hand, find the curves fit equally well when derived on other assumptions.

The I–P function of neither of the above authors has a term which would allow a decrease of ionization with pressure when higher pressures are reached. However, this decrease has been experimentally observed by Erikson[3] (not by Broxon,[8] however) so that the I–P relation is even more complicated than those derived by the above authors.

Obviously the intensity of ionization in a given gas is primarily dependent upon the source of ionization. If the source of ionization, or the gas in the ionization chamber, or the shielding is not changed and the ionizing radiation traverses the entire chamber with practically no diminution of intensity then the ionization per atmosphere at all pressures should be the same, and the I–P curve should be a straight line through the origin. Since this is not so, it is obvious that some of the above assumptions are not warranted, or that some other factor has to be considered. This additional factor is the recombination of ions in the chamber. This factor probably accounts for the departure of the curves from straight lines. If the slope of these curves at zero pressure and with saturation voltage could be determined, then the remainder of the experimental curve would be a measure of the incompleteness of saturation.

Practically all observers agree as to the form of the curves. In no case has a saturation current been produced. To show how the I–P curves fall short of saturation one could measure the slope of the curves at zero pressure, and draw a straight line with this slope from the origin. Theoretically these slopes for air, nitrogen and argon, when using gamma-rays, are in the ratios of their respective number of electrons per molecule.[10]

This ratio for argon and air is 18 : 14.4. This should represent the ratio of the slopes of the experimental curves at the origin. Since this slope could not easily be measured in these experiments, the slopes of the chords connecting the point at one atmosphere pressure with the origin was determined instead. The slope of the argon curve is 3.65×10^2 ions/cc/sec. per atmosphere, and that of air is 2.28×10^2, and the ratio of these is 18 : 11.25 which is much greater than the theoretical value given above. It is evident then that neither air nor argon shows saturation values, and that the loss of ions by recombination in argon is much less than in air. A comparative study of the gases can be made

[7] J. W. Broxon, Phys. Rev. **38**, 1704 (1932).

[8] J. W. Broxon, Phys. Rev. **37**, 1320 (1931).

[9] J. W. Broxon, Phys. Rev. **42**, 321 (1932) (abandons the above theory).

[10] Cf. Rutherford, *Radioactive Substances and Their Radiations*, p. 216, 1913.

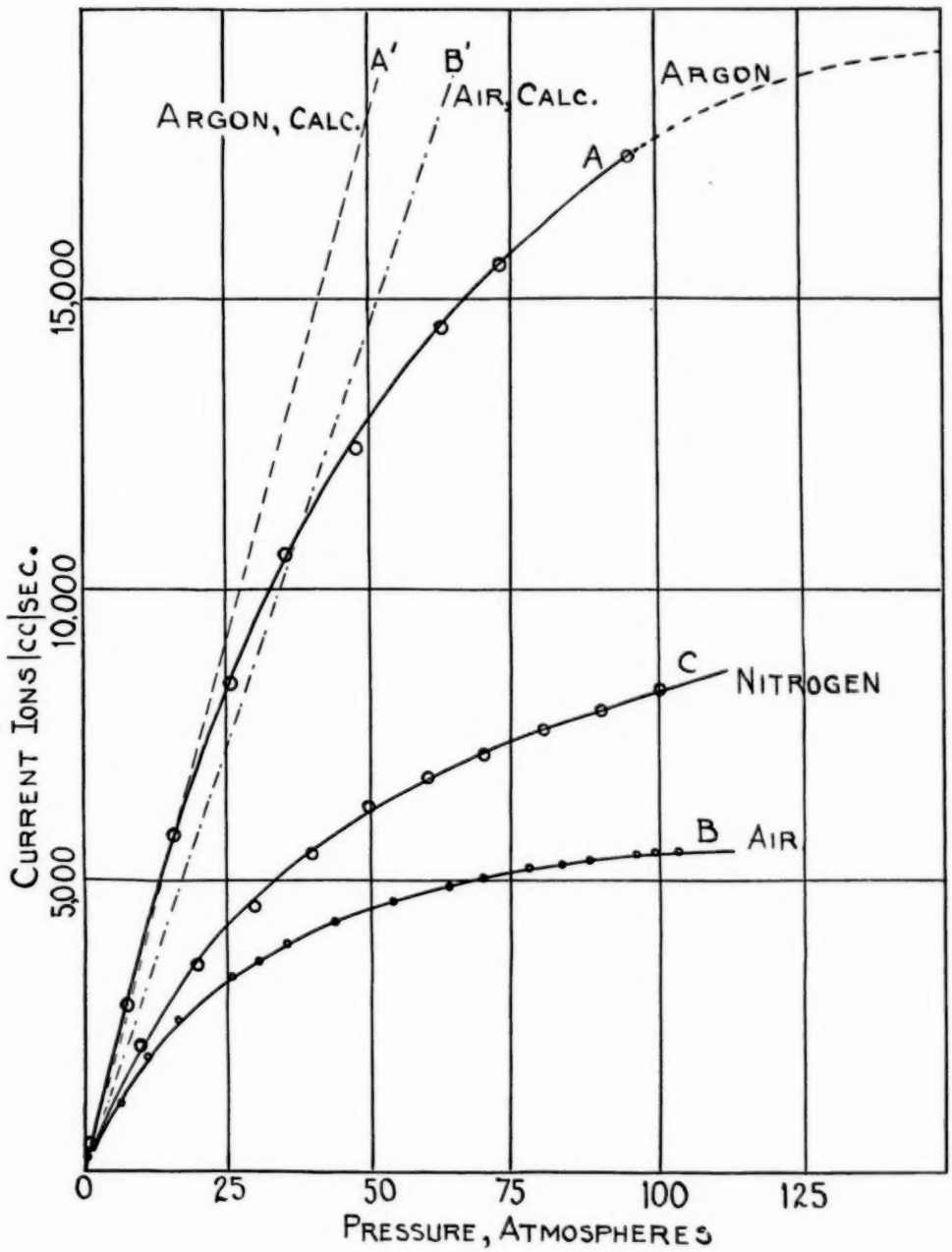

FIG. 6. Ionization-pressure curves of argon, air and nitrogen.

TABLE I. *Comparative ionizations in argon, air and nitrogen.*

1	2	3	4	5	6	7	8	9	10	11	12
p, (Atm.)	I, argon ions cm^{-3} $sec.^{-1}$	I/p, argon	I, argon (theor.)	Saturation percent argon	I, air ions cm^{-3} $sec.^{-1}$	I/p, air	I, air (theor.)	Saturation percent air	$\frac{I, \text{argon}}{I, \text{air}}$	I, nitrogen	$\frac{I, \text{argon}}{I, \text{nitrogen}}$
10	3.75×10^3	3.75×10^2	3.61×10^3	100.4	1.80×10^3	1.80×10^2	2.89×10^3	62.3	2.08	2.1×10^3	1.87
20	6.90	3.45	7.22	95.5	2.88	1.44	5.78	49.9	2.40	3.50	1.97
30	9.26	3.09	10.83	85.5	3.55	1.18	8.66	41.0	2.61	4.55	2.04
40	11.20	2.80	14.44	77.5	4.10	1.02	11.56	35.5	2.73	5.44	2.06
50	12.84	2.57	18.05	71.1	4.51	0.90	14.44	31.2	2.84	6.18	2.08
60	14.19	2.36	21.66	65.5	4.80	0.80	17.34	27.7	2.95	6.75	2.10
70	15.30	2.19	25.37	60.5	5.01	0.71	20.2	24.8	3.05	7.19	2.13
80	16.23	2.03	28.88	56.1	5.21	0.65	23.1	22.6	3.12	7.56	2.14
90	17.03	1.89	32.49	54.1	5.35	0.59	26.0	20.6	3.18	7.90	2.16
100	17.73	1.77	36.10	49.1	5.49	0.549	28.9	19.0	3.22	8.22	2.16
110	*(18.30)									8.46	
120	(18.70)									8.66	
130	(19.00)									8.80	
140	(19.14)									8.86	
150	(19.28)									8.92	
160	(19.30)									8.94	

* The values in parentheses represent an extrapolation of the argon values based on Broxon's data for nitrogen $f = 2.16$ was used.

with the slope of the argon I–P curve as a basis. The straight line A' representing this is drawn. The straight line for air B' is drawn with a slope 14.4/18 times this. Table I gives the results of this comparative study.

These curves and the table indicate the following things: (1) Curve A being more nearly linear than that of air B shows that a given voltage applied to the chamber produces a greater degree of saturation in argon than in air under the ionization of gamma-rays. (2) The greater height of the argon curve above either the air or nitrogen curves shows how much greater sensitivity can be expected from the use of argon in high pressure ionization chambers. (3) It is remarkable that the curves for argon and for nitrogen for the most part are similar (column 12). This makes it possible to extrapolate the argon curve by using the factor 2.16 to 150 atmospheres on the basis of Broxon's[7] data. These extrapolated values in the table are in parentheses. (4) The curves for air and argon are not similar (column 10).

The above data are offered with qualifications, namely: it was shown in a former section devoted to saturation current data that the same voltage does not produce the same degree of saturation at different pressures. Furthermore, although reasonable care was taken in filling the bomb with argon, nevertheless it was rated by the producers as containing 0.15 percent oxygen and 2.2 percent nitrogen as the chief impurities. The curve for pure argon should be slightly higher than this one.

IV. Current Lag on Filling Ionization Bomb

The bomb was newly filled with argon to 70.5 atmospheres pressure and the readings of ionization current with the radium at 1 meter were taken at intervals. Fig. 7 shows the results.

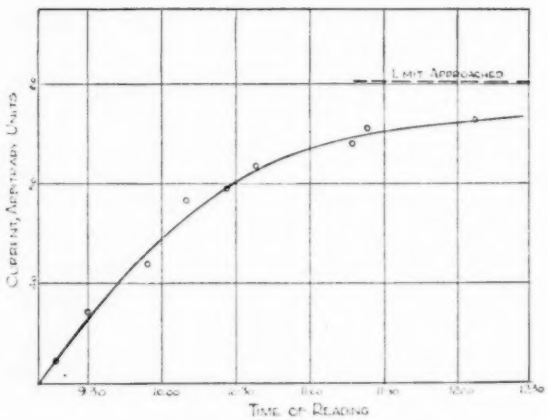

FIG. 7. Current change after filling the ionization chamber.

The current at first rises rapidly with the time. After three hours it is only 13.8×10^3 ions/cc/sec., whereas the end-current for this pressure is

14.3×10^3 ions/cc/sec. It takes about a day for the current to reach a constant value. It is for this reason that the data for the I–P curve with argon and with air were taken in the direction of decreasing pressure. The rise of current with time agrees with the results of Steinke and Schindler,[11] in CO_2, but is the reverse of the result of Broxon[9] in air, who found a decrease of current with time.

Evidently the cause of this lowered current is the dust from the walls and connection tubes and stopcock grease vapors torn loose by the rapidly moving gas. Until these particles have had time to settle out or move to the walls of the chamber they act as centers for clustering of ions where recombination of ions may readily take place. They also form ions of low mobility. Compton in a private communication states that a similar effect can be observed when the apparatus is first set up after being knocked about in transportation.

V. Recombination of Ions

Recombination of ions in air and in argon at low pressures have been extensively studied. (Erikson.[3]) Argon behaves in this respect like air. Figs. 8 and 9 show these data. The manner of obtaining them is as follows: the radium capsule was placed in contact with the unshielded bomb and was allowed to rest there until a large concentration of ions developed in the bomb, the field inside of the bomb being zero. The radium was then taken to a distance of two meters and placed behind 5 cm of lead. Since no field was applied at first, the concentration of the ions diminished chiefly by recombination. At a given time after removal of the radium, 10, 20, 30, etc., seconds, the 144 volt field was suddenly switched on and a fraction of a second later the key was opened so that the current to the electrometer could be measured. The data obtained in this manner are represented by the series of short curves of Figs. 8 and 9.

The manner of plotting these is best explained by taking as an example the data for the "40 seconds curve." The successive deflection readings on closing the key were 39, 49, 54, 59, 64. The average times elapsed between these respective deflection readings were 4.6, 4.45, 5.63 and 9.5 seconds. The sensitivity was 0.0615 volts/division. The successive currents calculated from these data are: 2.95, 1.53, 1.205 and 0.806×10^4 ions/cc/sec. The middle point of each of the above time intervals was chosen, so that the times to be plotted against the above currents are 42.3, 46.8, 51.8 and 59.4 seconds. The 40 seconds that has been added in each case is arbitrary. In like manner 30 seconds were added to the "30 seconds" readings, etc., so that these small curves are properly dispersed on a time scale. The heavy curves simply join like points of time elapsed after current readings were started on these smaller curves. The 5, 10 and 15 seconds points respectively are joined to make the larger graphs of curve 8, and the 10 seconds points to form the one of curve 9.

The striking thing shown by Fig. 9 is that this curve does not dip down to the line of constant current caused by ionization of the radium in its sheltered position but remains definitely above it. Take for example the last set of data which was taken after the ions had recombined for 10 minutes in zero field. These data can also be obtained from the reverse direction, i.e., starting with practically zero concentration of ions and allowing the radium to remain in its shelter for 20 or 30 minutes in the absence of a field. It is found that in this case the ionic concentration *builds up* to the values measured for the "10 minute curve." Thus, the current is about 10 times as great as the steady one with the radium in this position. This would seem to be a new method for temporary amplification of small currents. This phenomenon is obviously related to the long life of ions in argon.

VI. Mobility of Ions in Argon

Fig. 10 shows clearly that it takes some of the ions at least 50 seconds to traverse the ionization chamber, i.e., some of them move not faster than 1 mm/sec. These data were taken by first placing the radium against the ionization chamber but with the 144 volt field switched on, and the electrometer key closed. The current readings were taken by opening the key after the elapsed intervals of time indicated in the data.

[11] E. G. Steinke and Schindler, Naturwiss. **20**, 15 (1932).

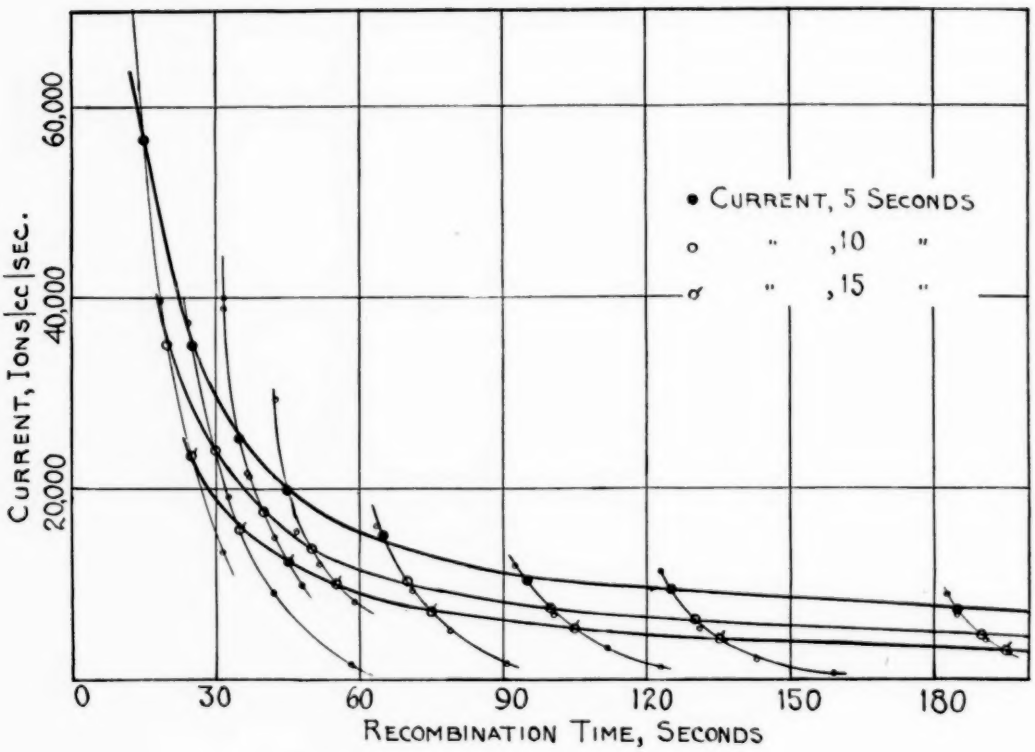

FIG. 8. Recombination of ions in zero field.

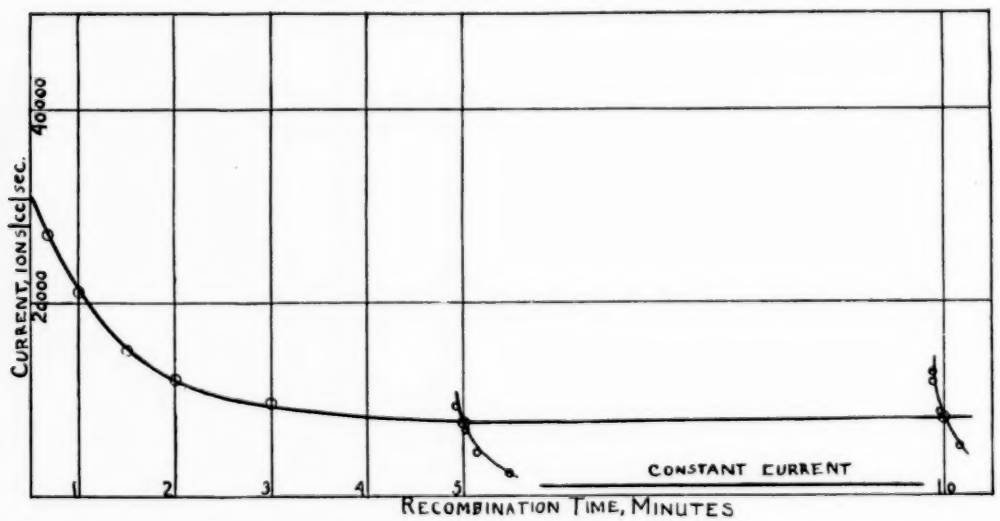

FIG. 9. Equilibrium concentration of ions in zero field.

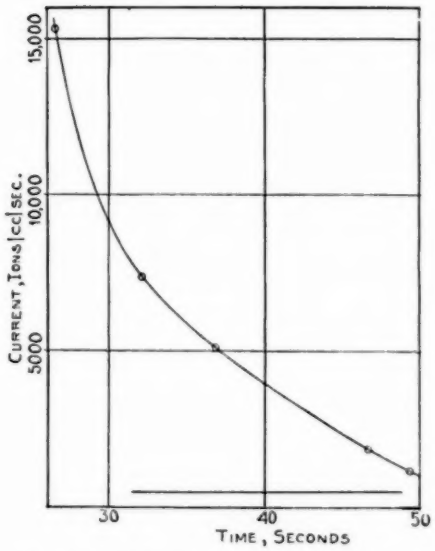

FIG. 10. Speed of the ions in the ionization chamber.

VII. INVERSE SQUARE LAW

After seeing what difficulty one has in measuring the real value of intensity of ionization or even of intensity ratios, one might think that the inverse square law of intensity could be used as an instrument for ironing out these difficulties. The study of this law simply showed up the more formidable difficulties already described in this paper. Moreover an additional variable was introduced, namely, the scattering of the rays from material near the apparatus, so that one cannot hope with these data alone to solve the problem which now involves intensity of radiation, lack of saturation voltage for the currents measured and the new factor of scattering bodies.

If one should make these experiments at low pressure of argon, where saturation voltages are easily possible, then any discrepancy in the inverse square law could be attributed to scattered radiation, and the percentage of this could be determined. If then a second experiment were made under the same conditions except with high pressure in the bomb, any additional discrepancy could be ascribed to nonsaturation voltage and the degree of this determined. Unfortunately, this could not be done in the present case. Compton suggested in a private communication that the effect of scattering could be largely eliminated by surrounding the bomb with lead. This has not been tried.

Many data were taken at several distances between 3 meters and 60 cm, but all values of n, the inverse square law exponent, were less than 2, and the greatest discrepancies occurred from the data taken at the smaller distances. The effect of scattering was easily observed by placing a plate of lead flat on the floor between the radium and the ionization chamber. The ionization current was increased perceptibly thereby.

VIII. MEASURING COSMIC RAYS

In using the instrument for measuring cosmic rays relative to gamma-rays from radium, three measurements are necessary besides a determination of the constants of the instrument. The three measurements are: (1) Current due to cosmic rays plus local radiation through two shields of lead and one of bronze.[1] (2) Current due to gamma-rays from radium in a standard position plus cosmic rays plus local rays through two shields of lead and one of bronze. (3) Current due to cosmic rays plus local rays through one lead shield and the bronze shield.

The equations necessary to evaluate the intensity of cosmic radiation and the ratio of this intensity to the radium standard are the following:

$$a = x_1 + x_2 \quad (1) \qquad d = x_2/x_5 \quad (4)$$

$$b = x_1 + x_2 + x_3 \quad (2) \qquad e = x_1/x_4 \quad (5)$$

$$c = x_4 + x_5 \quad (3)$$

where x_1 = current due to cosmic rays through shields 1, 2 and 3; x_2 = current due to local rays through shields 1, 2 and 3; x_3 = current due to gamma-rays from radium in standard position through shields 1, 2 and 3; x_4 = cosmic rays through shields 1 and 2 (one bronze and one lead shield); x_5 = current due to local rays through shields 1 and 2; a, b and c are the electrometer currents already described in sentences numbered 1, 2 and 3 above; $\alpha = 0.94$ and $\alpha^d = 0.312$, the constants of the lead shields for cosmic rays and local rays, respectively. The value of d was deduced from measurements made by Compton. The value of e was determined for gamma-rays from radium. The application of the same constant to the local radiation seems to be reasonable.

The above five equations can be solved simultaneously for the five x's. However we are interested here only in x_1, x_3 and their ratio. The solution gives:

$$I_c = x_1 = [e/(e-d)](a-dc) \quad (6)$$

$$I_r = x_3 = b-a \quad (7)$$

$$I_c/I_r = x_1/x_3 = [e/(e-d)](a-dc)/(b-a). \quad (8)$$

Eq. (8) can be transformed into Compton's equation for measuring the ratio of cosmic rays to gamma-rays.

Substituting the numerical values of d and e in Eqs. (6) and (8) gives the following result:

$$x_1 = 1.497(a-0.312c) \quad (6a)$$

$$x_1/x_3 = 1.497(a-0.312c)/(b-a). \quad (8a)$$

Substituting the numerical values of a, b and c in Eqs. (6a), (7) and (8a) the values in Table II result. In this table, a, b, c and the x's are in the same arbitrary unit of current.

TABLE II.

No.	a	b	c	$I_c=x_1$	$I_r=x_3$	I_c/I_r	Place, Material
1	0.1019	0.740	0.122	0.0956	0.6381	0.1499	Eckhart Hall Air, 36 atm.
2	.1338	.790	.1740	.1190	.6562	.1815	5430 Univ. Ave. Air, 36 atm.
3	.405	3.04	.511	.368	2.645	.1390	Eckhart Hall Argon, 73.6 atm.
4	.256	2.21	.329	.230	1.954	.1176	Eckhart Hall Argon, 36 atm.

On comparing the data for the two pressures of argon, the x_1's and the x_3's, it is found that they do not change in the same ratio. Thus[12] $(3)x_3/(4)x_3 = 1.35$, whereas $(3)x_1/(4)x_1 = 1.60$. These ratios should be the same if a saturation current is obtained, or if the same degree of saturation is produced in both cases. The ratio is greater for the x_1's than for the x_3's, which is in accordance with the expectation that the increase of ionization current is more nearly proportioned to pressure for the weaker source of ionization. Figs. 1–4, on the other hand, indicate that the ratio of current to pressure passes through a maximum for certain current values indicating a slight residual ionization, probably due to radioactive material in the chamber.[9]

If one compares the results of air and argon at the same pressure and the cosmic-ray intensity at the same place, namely Nos. 1 and 4, then $(4)x_1/(1)x_1 = 2.41$, and $(4)x_3/(1)x_3 = 3.06$. That is the ratio of increase in ionization when the monatomic gas is used in the ionization chamber is much greater for gamma-rays than for cosmic rays. A suggested explanation for this difference is that the air contains more radioactive contamination than argon. Another is in the possibility that the primary attack of cosmic rays is on atomic nuclei, while the gamma-rays act chiefly on extranuclear electrons. The interaction of cosmic rays and atomic nuclei has already been suggested by experiments of Millikan and Anderson.[13] Since argon has half as many nuclei as air at the same pressure a smaller ratio (2.41) for cosmic rays than for gamma-rays (3.06) should be expected for it. It is seen that these data are quite in accord with this view. This, I believe, is the first direct comparison of the action of cosmic rays on monatomic and diatomic gases.

This work was supported by funds from the Carnegie Institution, and carried out at the University of Chicago under the direction of A. H. Compton.

[12] $(3)x_3$, etc., indicates the x_3 of measurement No. 3 of Table II.

[13] R. A. Millikan and C. D. Anderson, Phys. Rev. **40**, 1056A (1932).

Fluctuations of Cosmic-Ray Ionization

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The cosmic-ray ionization in air contained at a pressure of 157.5 atmospheres in the 13.8 liter steel chamber surrounded by the 5.5–6 ft. water shield as previously described, was measured at four-hour intervals during a period of fifteen consecutive days, April 6–20, 1932. Controlled laboratory conditions and compensation features of the measuring equipment contributed to the constancy of measured ionization values. By means of recording instruments, simultaneous records of the atmospheric potential gradient, the atmospheric temperature, the barometric pressure, and the relative humidity were also secured. It was determined that a decrease of 2.1 percent in the cosmic-ray ionization corresponded to an increase of 1 cm in the barometric column. No correlation was established between the ionization and the atmospheric potential gradient, the atmospheric temperature, or the absolute humidity. There appeared to be no regular diurnal variation of the ionization either before or after the application of corrections for variations in barometric pressure. When deviations from the average of the ionization values corresponding to a particular time of day were regarded as statistical fluctuations, the average probable error so calculated was 0.21 percent. The greatest difference between the grand average and the average ionization for a particular time of day was only about one-third of one percent, less than twice the probable error. It seems very likely that the fluctuations observed were of a statistical nature.

IF the intensity of the primary penetrating radiation varies in a regular manner with definite periodicities, the detection of these should provide valuable indications as to the origin of the radiation. If fluctuations of the radiation intensity could be correlated with variations in specific atmospheric conditions, further inferences regarding the origin and possible nature of the radiation might be expected to result. This situation has long been realized and numerous studies[1] of the fluctuations of the residual ionization in closed vessels were made even during the early stages of the investigation of the radiation. The conclusions of investigators were varied, there being no general agreement as to whether or not regular fluctuations not attributable to laboratory conditions actually existed, or as to their single or double diurnal periodicity if they did exist.

With progress in the study of the penetrating radiation it has been possible to improve the conditions of measurement of the ionization produced, to eliminate certain disturbing influences, and to estimate better to what extent actual fluctuations in the intensity of the penetrating radiation may have been detected. In spite of refinements of measurement, however, the most recent researches have led to conclusions nearly as much at variance among themselves as was the case in the early period of investigation, although fluctuations on a smaller scale are now being investigated. Hoffmann[2] has recently summarized very briefly the contents of 57 papers on the subject, published during the last decade by 19 investigators. These investigators differ widely in their conclusions regarding the existence, nature, and causes of the fluctuations, and the inferences to be deduced from them.

The following examples illustrate the lack of agreement still existing. Steinke[3] initially found the ionization intensity essentially constant, but later[4] detected a periodicity according to sidereal time even at sea level. Hess and Pforte[5] have noted a regular maximum at about noon and have concluded that an appreciable portion of the primary radiation originates in the sun. Millikan[6] observed a maximum in the early afternoon and attributed it to decreased shielding

[1] See references 11 to 18, incl., Phys. Rev. **27**, 552 (1926).

[2] G. Hoffmann, Phys. Zeits. **33**, 633 (1932).

[3] E. Steinke, Zeits. f. Physik **42**, 570 (1927).

[4] E. Steinke, Phys. Zeits. **30**, 767 (1929); Zeits. f. Physik **64**, 48 (1930).

[5] V. F. Hess, Nature **127**, 10 (1931); V. F. Hess and W. S. Pforte, Zeits. f. Physik **71**, 171 (1931).

[6] R. A. Millikan, Phys. Rev. **36**, 1595 (1930).

of the atmosphere not represented by alteration of the barometric pressure. Since then he has pointed out that the earlier measurements, particularly those at high altitudes, were affected by fluctuations of temperature of the ionization equipment, and concludes from more recent measurements[7] that there are no regular fluctuations exceeding $\frac{1}{3}$ percent. Although he appears rather in doubt as to the reality of these, he considers that if they do exist, his explanation is correct. Bennett, Stearns and Compton,[8] although at first considering no regular fluctuations existed, concluded after applying corrections for changes in barometric pressure and variations of battery e.m.f. with temperature, that at an altitude of 3900 m (and at a station distant less than 36 miles from the University of Colorado campus) there was a regular diurnal variation with an amplitude of the order of one percent, and with a maximum at about noon. They attributed the variations to an excess of penetrating radiation originating in space in the neighborhood of the sun. Gunn[9] has offered an explanation of these fluctuations in terms of diurnal fluctuations of the terrestrial magnetic field, assuming the radiation to be corpuscular in nature, in accordance with Compton's[10] conclusions as to variations with latitude. Messerschmidt[11] has concluded that the intensity of the primary penetrating radiation is constant, but has observed regular diurnal fluctuations of the ionization measured with only laterally shielded apparatus, and together with Hoffmann[12] has correlated them with the temperature of the atmosphere. He concludes that the observed variations are due to fluctuations in the intensity of subsidiary radiations generated in the neighborhood of the ionization chamber. Mott-Smith and Howell[13] have investigated the ionization due to penetrating radiation at altitudes up to 27,000 ft. They found "no significant decrease in intensity . . . during the night-time observations even at the highest altitudes."

In view of the continued lack of agreement regarding fluctuations of the penetrating radiation intensity as inferred from ionization measurements, it was decided to make a series of observations of the cosmic-ray ionization at regular intervals with very carefully controlled laboratory conditions. Because of their possible relation to the ionization values, simultaneous values of the barometric pressure, the outdoor atmospheric temperature, the humidity of the atmosphere, and the atmospheric vertical potential gradient were also recorded.

Procedure

Details regarding the equipment used in measuring the cosmic-ray ionization have been described by the senior author.[14] This same equipment, with the identical air used in a recent determination[15] of the ionization—temperature effect at high pressures, was employed during the present investigation. With its very thorough guard system and its compensation features eliminating effects of variations of electrometer sensitivity and of the P.D. impressed across the ionization chamber, this equipment, closely resembling that designed by Professor Swann,[16] was remarkably well adapted to an investigation extending over a considerable time interval.

Not only were fluctuations of ionization values due to several possible sources eliminated by the method of measurement, but controlled laboratory conditions eliminated other possible local causes of variations. With the indoor location and the $5\frac{1}{2}$–6 ft. water shield[14] about the ionization chamber, the gradual variation of the temperature of the chamber amounted to less than 1°C during the entire 15-day period of the measurements. The temperature effect having been investigated under these specific conditions, the temperature correction, although practically negligible, could be made. The gas content of the ionization chamber was found to remain con-

[7] R. A. Millikan, Phys. Rev. **39**, 391 (1932).

[8] R. D. Bennett, J. C. Stearns and A. H. Compton, Phys. Rev. **41**, 119 (1932).

[9] R. Gunn, Phys. Rev. **41**, 683 (1932).

[10] A. H. Compton, Phys. Rev. **41**, 111 (1932); Phys. Rev. **41**, 681 (1932).

[11] W. Messerschmidt, Zeits. f. Physik **78**, 668 (1932).

[12] G. Hoffmann, Zeits. f. Physik **69**, 703 (1931).

[13] Lewis M. Mott-Smith and Lynn G. Howell, paper presented at Atlantic City meeting, December, 1932. See Phys. Rev. **43**, 381 (1933).

[14] J. W. Broxon, Phys. Rev. **37**, 1320 (1931).

[15] J. W. Broxon, Phys. Rev. **42**, 321 (1932).

[16] W. F. G. Swann, J. Franklin Inst. **209**, 151 (1930).

stant not only during the period of this investigation, but for considerable intervals before and after. Even had some leakage occurred, previous work has shown that the effect would have been negligible at the pressure (157.5 atmospheres) employed. Former work had shown that at the pressures employed any possible contribution to the ionization by radioactivity of the chamber or its contents was negligible. Consequently, no fluctuations could arise on this account. Moreover, the heavy shield very effectively cut off possible gamma-radiations from external sources, thus eliminating the possibility of fluctuations due to variations in the emanation content of the atmosphere.

Six series of observations were made at regular intervals each day for fifteen consecutive days, April 6–20, 1932. One such series was begun at about 1:00 A.M. After the P.D. of about 875 volts had been impressed across the ionization chamber for at least 15 minutes, an ionization current observation was made in the usual manner, the interval during which charges were collected being about eight and one-half minutes in duration. Usually three, but occasionally two or four such observations were made in fairly rapid succession. Normally the series of observations was completed before 2:00 A.M. Such a series of observations has been considered to represent the ionization at 1:30 A.M. In this manner the value of the ionization current was determined at 1:30 A.M., 5:30 A.M., 9:30 A.M., 1:30 P.M., 5:30 P.M., and 9:30 P.M. each day. On only two occasions did considerable departures from this procedure inadvertently occur: the 1:30 P.M. readings on April 6 were actually made between 1:18 and 3:08 P.M., and the 1:30 P.M. readings on April 18, between 2:01 and 2:25 P.M.

All ionization measurements were made by the authors. As far as feasible, the observations made during a particular day, as well as those made at a particular time of day during the 15-day period, were distributed equally among the three observers.

The atmospheric potential gradient was obtained from equipment installed in a building on the University campus. This equipment yielded continuous photographic records, and a reduction factor was determined which gave absolute values of the potential[17] at a point one meter above the surface of the earth. The equipment was not in operation during about four of the fifteen days.

The relative humidity and the temperature of the atmosphere were obtained from recording instruments of the Department of Geology, located in an outdoor "shelter house." From these the absolute humidity was calculated. With the exception of a few readings, the atmospheric pressure was obtained from a Short and Mason (London) micro-barograph operated by the Mechanical Engineering Department. The barometric pressure values from 5:30 P.M., April 16 to 5:30 A.M., April 18, inclusive, were obtained from a less sensitive Geology Department barograph.

Observations

Certain significant relations among the data have been represented graphically. From the observed ionization values, "corrected" ionization values were obtained by reduction to the average ionization chamber temperature of 17.42°C by application of the minute temperature corrections in accordance with previous determinations, and by reduction to the average barometric pressure of 24.73 inches in accordance with the observed dependence upon barometric pressure to be discussed later. The observed ionization values are shown plotted against the barometric pressure in Fig. 1. In this diagram 1:30 A.M. readings are designated by 1A; 5:30 A.M. readings, by 5A; 1:30 P.M. readings, by 1P, etc., all of which refer to Mountain Standard Time. Both observed and corrected ionization values are plotted against the outdoor temperature in Fig. 2; corrected ionization values, against absolute humidity (as determined from the atmospheric temperature and the relative humidity) in Fig. 3; and corrected ionization values, against the atmospheric potential gradient in Fig. 4. It was considered that this treatment would make a possible relation between the ionization and any of the measured atmo-

[17] A study of the local atmospheric potential gradient determined more or less continuously over a period of more than a year has been made. It is hoped to have the results of this investigation ready for publication in the near future.

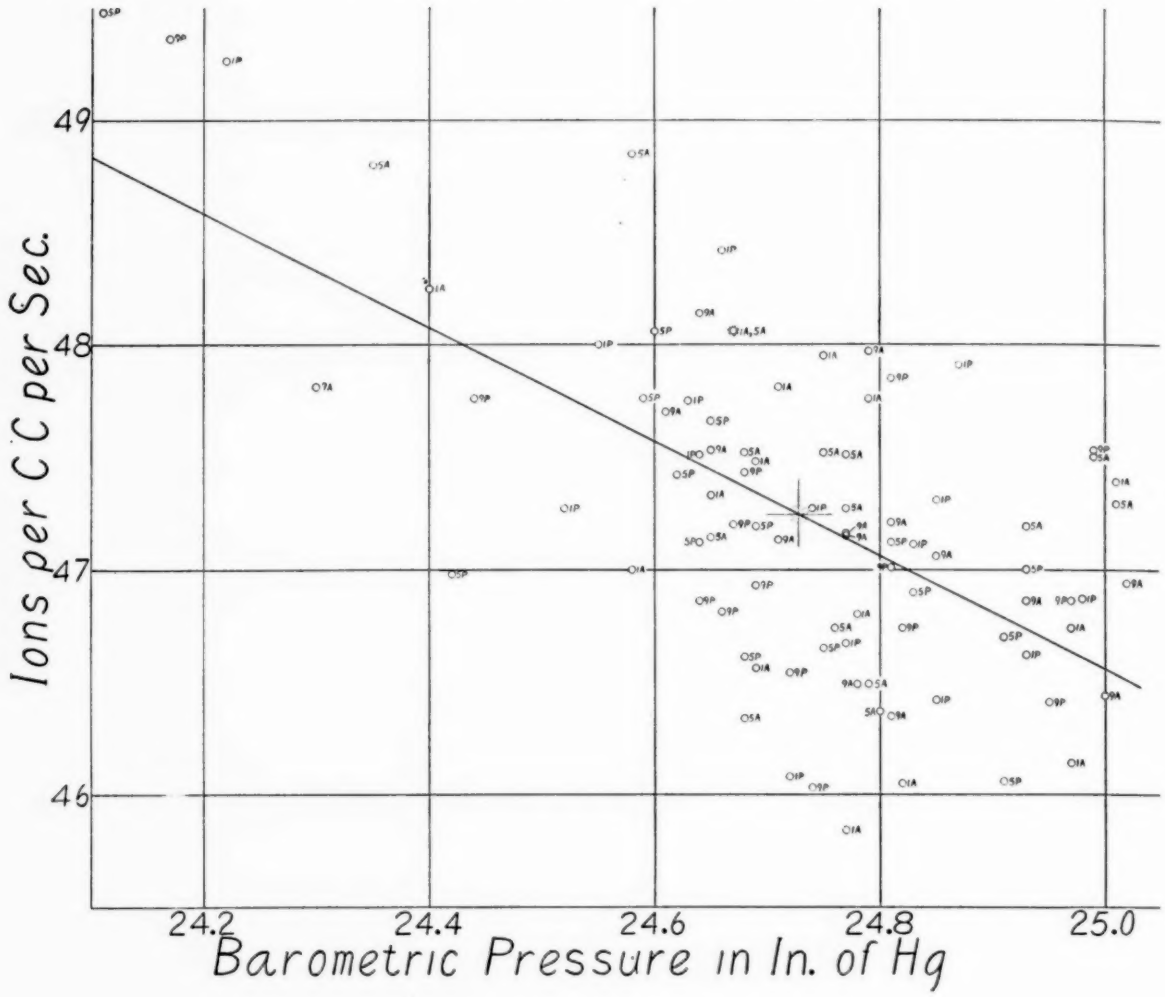

FIG. 1. Observed ionization plotted against barometric pressure.

spheric characteristics more readily apparent than would the construction of neighboring curves showing the variation of each of these with time in the usual manner. For a similar reason the ionization-time curves for the fifteen days are shown superimposed in Fig. 7, in preference to a continuous small-scale time curve extending over the entire period.

DISCUSSION

An inspection of Fig. 1 discloses a definite dependence of the cosmic-ray ionization upon barometric pressure, an increase in atmospheric pressure resulting in general in decreased rate of production of ions. This is in general agreement with the results of various investigations made during the last several years, both in relation to the direct barometric effect at a given location, and to the variations of ionization with altitude. The rather wide distribution of points probably may be attributed to the short duration of the individual ionization current measurements, and to the small range of atmospheric pressures involved.

Assuming a linear relation between the ionization and the barometric pressure, the slope of the line was determined by the method of least squares to be $dI/dp = -2.526$ ions per cc per sec. per inch of mercury, using the 90 values plotted. With only the 1:30 A.M. values, then only the 5:30 A.M. values, etc., the slopes ob-

tained were −2.295, −2.403, −1.985, −2.970, −3.043, −2.461, in the order given. Since each of these slopes corresponding to a particular time of day depended upon only 15 values, and because of the small range of the variations involved, the agreement among them is considered rather good. It is concluded, therefore, that the ionization-barometric pressure relation is direct rather than due to variations of each with the time of day. The average of the six 15-point slopes, equal to the 90-point slope and designating a decrease of 5.3 percent in ionization per inch (2.1 percent per cm) increase in the barometric column, is considered adequately to represent the ionization-barometric pressure relation under the actual conditions of measurement.

To have determined from the observations of other experimenters the barometric effect to be expected in the present instance would have been difficult because of the shielding arrangement, particularly the irregular shielding offered by the building in which the equipment was located. A rough comparison with the observations of others may be effected by reversing the procedure, however. The observed variation of 2.1 percent in ionization per cm change in the barometric column is apparently nearly coincident with that defined by the slope at sea level of the ionization-altitude curve obtained by Millikan and Cameron[18] with a 3 mm-wall steel ionization chamber surrounded by a 7.64 cm lead shield. Not only the barometric effect but also the absolute value of the ionization determined by them at sea level (27.90 ions/cc-sec. at 20 ft.) is nearly equal to the 26.7 ions/cc-sec. previously measured[14] in the present heavily shielded ionization chamber at its altitude of 5400 ft. and at the pressure of 30 atmospheres used by Millikan and Cameron. The variation with barometric pressure is also slightly greater than the 1.92 percent change in ionization per cm change in the barometric column observed by Messerschmidt[11] at Halle (altitude, 110 meters) with an ionization chamber surrounded on all sides by a 10 cm lead shield, the top of the shield having been removed.

[18] R. A. Millikan and G. H. Cameron, Phys. Rev. **37**, 235 (1931).

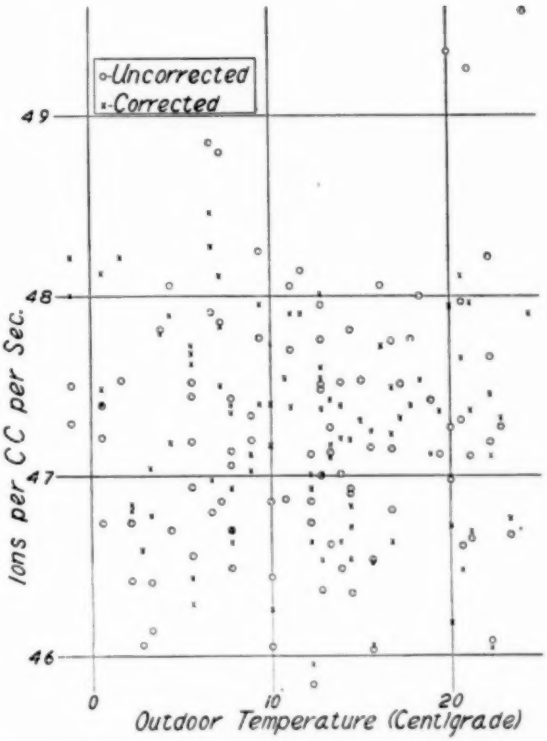

FIG. 2. Observed and corrected ionization values plotted against outdoor temperature.

Figs. 2, 3 and 4 do not show any decided relation between the cosmic-ray ionization and the atmospheric temperature, the absolute humidity, or the atmospheric potential gradient. In Fig. 2 are included two sets of points, one designating observed ionization values, and the other indicating the corresponding values after reduction to the average barometric pressure and ionization chamber temperature. All values shown in Figs. 3 and 4 have been so reduced.

On the basis of the observations of Hoffmann[12] and Messerschmidt[11] there might have been anticipated some relation between the ionization and the atmospheric temperature even though the ionization due only to the softer portion of the incident cosmic radiation varied with the temperature, since as shown above, in the present work the total shielding against radiation from outside the atmosphere was probably comparable to that offered in the case of Messerschmidt's measurements at Halle with the top of the lead shield removed. If their explanation is correct, however, and the dependence upon

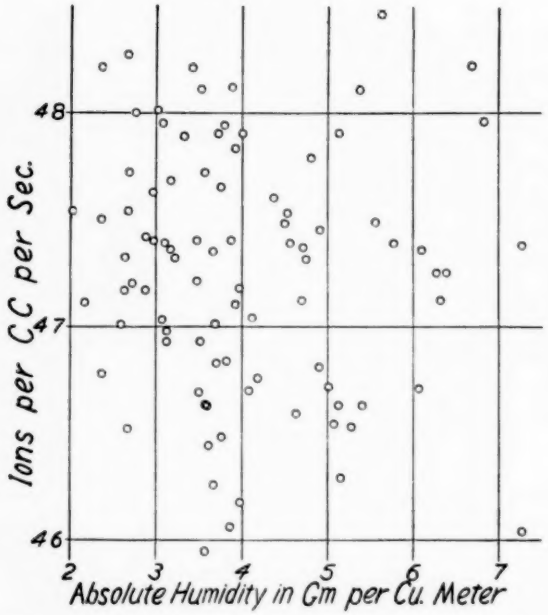

FIG. 3. Corrected ionization values plotted against absolute humidity.

atmospheric temperature occurs only through the agency of subsidiary radiations generated locally in materials of varying temperature, then in the present equipment with its very heavy constant-temperature shield, it is not surprising that no relation between the ionization and the outdoor temperature was observed.

In view of the dependence of the ionization upon the barometric pressure, it would seem there might also be a dependence upon the water content of the atmosphere. The absolute humidity is likely to be a rather local affair, however, and is probably not representative of the water vapor content of the atmosphere at considerably different altitudes. Consequently, a random distribution such as that shown in Fig. 3 was not wholly unexpected.

The likelihood of a dependence of the cosmic-ray ionization upon the atmospheric potential gradient would depend upon the nature of the radiation and perhaps upon the extent to which the gradient at the earth's surface is representative of electrical conditions at higher altitudes. According to Fig. 4 no specific relation of this type appears to have been disclosed by the present investigation. However, it is noticeable that the largest potential gradient values occur in connection with ionization values in the neighborhood of the mean. It is regrettable that more data of this variety were not secured.

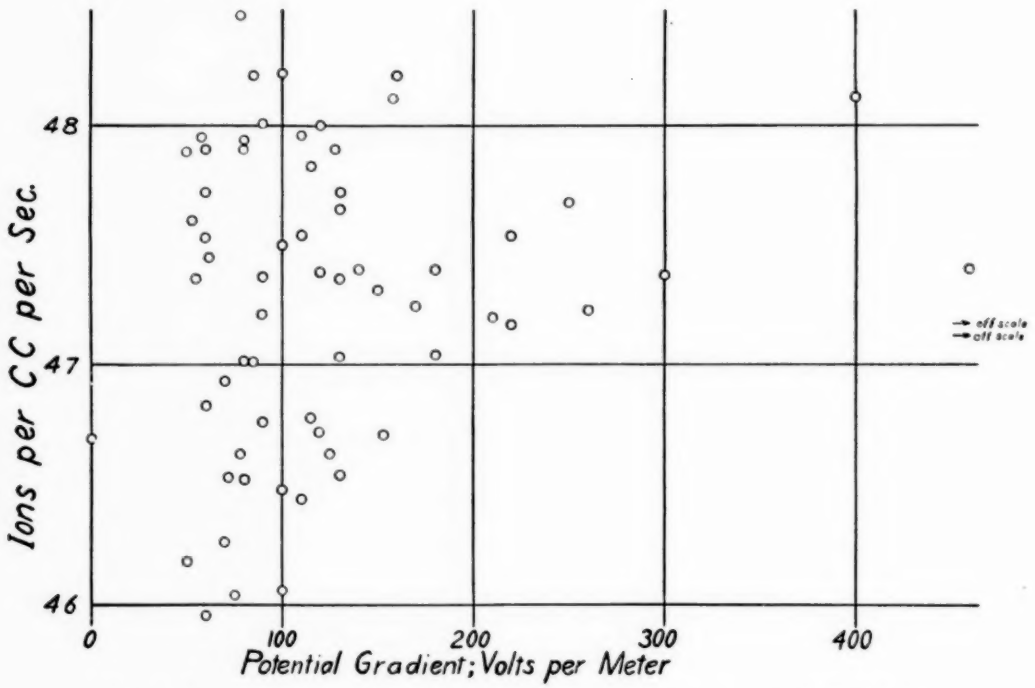

FIG. 4. Corrected ionization values plotted against atmospheric potential gradient.

It should be emphasized that only first order relations would be made apparent by the Figs. 1–4. Could the others have been maintained constant, the dependence of the ionization upon a particular one of the four additional variables investigated might have been made apparent. To enable one to test this possibility adequately a much larger number of observations should have been available, from which special classes could have been selected. However, a certain attempt in this direction was made. In Fig. 3 it will be noted that a large fraction of the observations correspond to absolute humidities in the limited range between 3 and 4 g per cu m. When the observations corresponding to these were selected, there was still no apparent relation between the ionization and either the atmospheric temperature or the potential gradient, with the humidity so restricted.

Fig. 5 illustrates the dependence of the ionization upon the time of day. The average of the

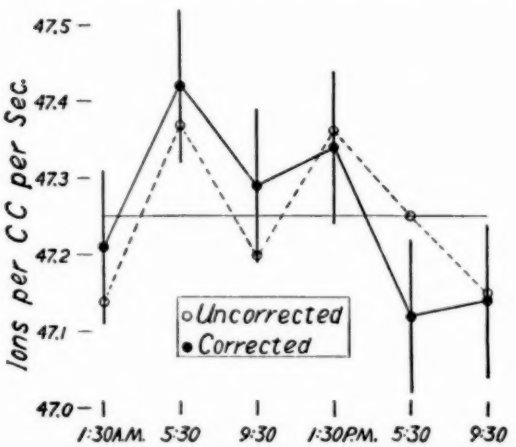

FIG. 5. Dependence of ionization upon the time of day.

ionization values at a particular time of day during the entire 15-day period is here shown as a function of the time. The averages of both observed and corrected values are designated by the two sets of circles. In an attempt to determine the significance of the curves obtained in this manner, the probable error of the corrected ionization values at a particular time of day was determined on the basis of the differences between these values and their average. In this manner the probable errors were found to be 0.12, 0.11, 0.08, 0.10, 0.08, 0.11 ions/cc-sec. for the 1:30 A.M., the 5:30 A.M., etc., readings in the order given. The average of these, 0.10, amounts to 0.21 percent of the grand average ionization (corrected) of 47.25 ions per cc per sec. Vertical lines have been drawn through the points designating average corrected ionization values, extending above and below the points a distance equal to the average probable error. It is apparent that three of these values differ from the grand average by less than the probable error, two by just a trifle more, and even the 5:30 A.M. average which departs most from the grand average differs from it by less than twice the probable error. The curve obtained without the application of the barometric pressure and ionization chamber temperature corrections is seen to lie rather nearer the average than the corrected ionization curve.

It should be mentioned that in obtaining these curves the ionization at a particular time on a particular day was considered to be represented by the arithmetical mean of the individual eight-minute observations obtained during the corresponding interval as described above, irrespective of whether 2, 3, or 4 such individual observations were made. It was found that weighting these initial averages in proportion to the number of eight-minute observations from which they were obtained produced no appreciable alterations in the final corrected ionization-time curve of Fig. 5. Because of this fact, and because no other method of obtaining values representative of such small numbers of individual readings appeared justifiable, the unweighted averages have been employed throughout. Upon application of the Chauvenet criterion to the individual eight-minute observations, it was found that only one of these should be considered improbable. The average of the group of four in which it occurred satisfied the criterion. Consequently, none were rejected.

To test further the likelihood that fluctuations of the averages shown by Fig. 5 occurred by chance, the averages for the three successive five-day intervals were determined, and are shown in Fig. 6. It is seen that there are no general similarities among the three curves. Similarly, the averages of the ionization values determined at particular times of day by a particular observer were also calculated, and the

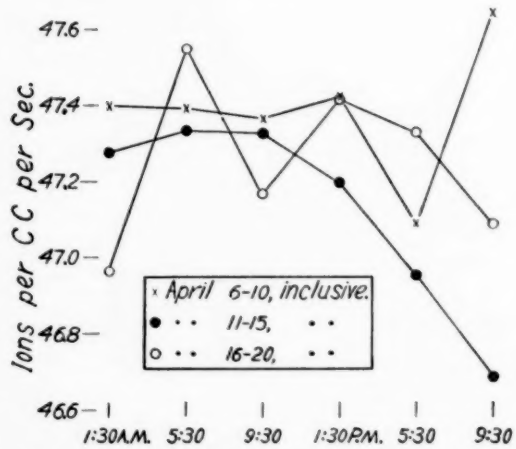

FIG. 6. Average ionizations for three successive five day intervals.

three ionization-time curves (not shown) corresponding to the three observers were found to have no apparent common characteristics. Incidentally, the respective probable error of each observer, calculated on the basis of deviations from the average of his own ionization values, was smaller than those recorded above.

The ionization-time curves for the individual days, shown superimposed in Fig. 7, constitute a rather complicated diagram, but they show that no particular type of diurnal variation is reproduced with any considerable regularity on several days.

In view of the above considerations and the further fact that the maximum of the average ionization values of Fig. 5 occurs at 5:30 A.M. whereas other experimenters who have detected a diurnal variation agree rather well on a maximum at about noon or in the early afternoon, it is concluded that the fluctuations observed were probably statistical in nature and that no regular diurnal variation of the cosmic-ray ionization capable of being detected with the equipment used can be considered to have existed under the conditions of measurement. Not only was no regular diurnal variation observed, but there appeared to be no appreciable dependence of the ionization upon the atmospheric potential gradient, the outdoor temperature, or the absolute humidity, while the dependence upon barometric pressure was in good accord with that observed by others.

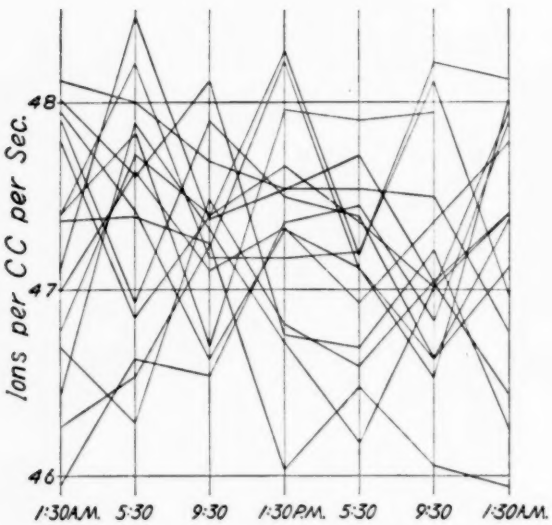

FIG. 7. Ionization-time curves for individual days.

Relative to the "sudden increases" or "bursts" of ionization occasionally observed and previously[15] mentioned, it is perhaps worth remarking that seven instances of these appear to have occurred during the 41.1 hours occupied by the 291 readings distributed over the 15-day interval. (Of these, five were detected by one observer, and only one by each of the others.) On the other hand, during a nearly continuous series of measurements which occupied 20.4 hours of the interval from 10:00 A.M. April 29 to 10:00 A.M. April 30, only one such occurrence was observed. (About nine minutes of each hour were taken for resetting apparatus.) The average rate of occurrence of one "burst" in six hours in the first interval and one in twenty hours in the second instance can have only slight significance in view of the short intervals involved. However, the observations do give some indication as to the order of magnitude of their frequency, in surprising agreement with the very much more reliable determinations of Steinke and Schindler[19] and of Messerschmidt[11] by continuous observations extending over vastly longer time intervals.

The writers gratefully acknowledge their indebtedness to Professor J. A. Hunter of the Mechanical Engineering Department and Professor H. A. Hoffmeister of the Geology Department for supplying the charts mentioned above.

[19] E. Steinke and H. Schindler, Zeits. f. Physik **75**, 115 (1932).

Cosmic-Ray Intensities in the Stratosphere

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Three flights which reached altitudes, according to official weather bureau records, corresponding to the barometric pressures 79 mm, 32 mm, and 16 mm of mercury respectively are reported. In two of these flights dependable electrometer readings down to pressures of 88 mm and 61 mm, respectively, are obtained. These flights enable a *weighted mean* ionization-altitude curve to be obtained down to a pressure of 61 mm or 92 percent of the way to the top of the atmosphere. The same shape of the ionization-altitude curve is obtained from both flights and also from the flights made by Regener and by Piccard. This shape is concave downward at the top, i.e., it shows a decreasing absorption coefficient as the top is approached. This indicates non-ionizing primary entering rays not yet wholly in equilibrium with their secondary particle rays. The absolute values of the ionization found in each of these two flights and on Regener's flight are in agreement within the limits of observational uncertainty.

I. The Problem

THE study of the ionization produced by the cosmic radiation in the upper layers of the atmosphere, i.e., in a region far above that accessible by airplanes or manned balloons, is of so much importance for the determination of the nature and origin of these rays that during the past summer we undertook again to attack this problem by the method which we first initiated in 1922;[1] namely, by sending up recording electrometers, barographs, and thermometers in sounding balloons and studying the records brought back to earth in parachutes, or otherwise.

II. The Instruments

The determinations of both pressures and temperatures were made by the Weather Bureau, which generously undertook this whole enterprise in cooperation with ourselves and placed their men, their facilities, and their experience at our disposal. The meteorographs used were the regular Fergusson Weather Bureau sounding balloon instruments made by Julian P. Friez and Sons, Baltimore, and the altitudes were worked out from these records by the Weather Bureau staff at Washington. The electrometers were of our own design, and were along the general lines of our 1922 instruments.[1] They were made by the machine shop force of the California Institute of Technology, the sensitive quartz systems, however, being built by Dr. H. V. Neher. These instruments, however, were larger than those used in 1922, being steel cylinders 10 cm in diameter and of walls 0.3 mm thick, provided with conical ends, the whole capacity being about 1165 cc. They could be filled with gas up to a pressure of four atmospheres through a needle valve in the bottom end. Actually the best flight herein described was made with a pressure of 4 atmospheres, while the second one corresponded to a pressure of 2.2 atmospheres. The quartz system was of the usual Wulf two-fiber type, differing from those which we have regularly used only in that the lower supporting fiber was not made as stiff as usual so that the restoring force resided chiefly in the stiffness of the recording fibers themselves. This modification was made to reduce the effect of temperature to a minimum and the success attained is shown by the fact that the electrical constants of the system were found to vary less than 2 percent when the temperature rose from $-77°C$ to $+23°C$. The mechanism for charging the fibers was operated by an electromagnet which acted through the thin steel wall of the small hollow cylinder at the top upon an iron plunger inside so that the operation of charging could not in any way endanger the air-tightness of the vessel. Fig. 1 is a photograph of one of the

[1] R. A. Millikan and I. S. Bowen, Phys. Rev. **27**, 353–361 (1926); *Millikan Carnegie Institute Year Book* **21**, 385 (1922).

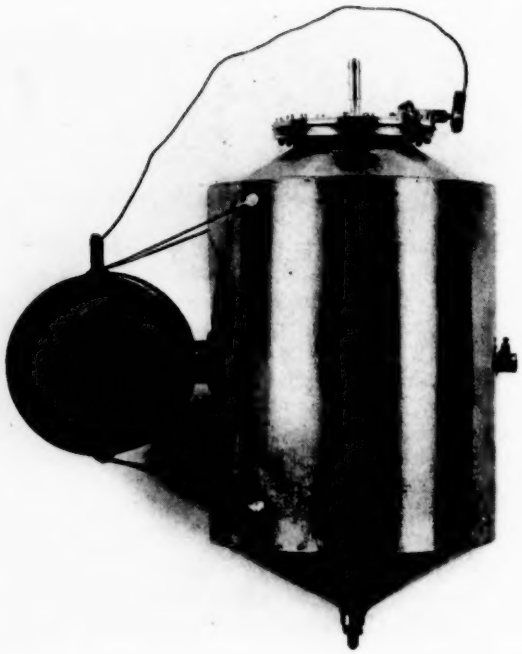

FIG. 1. Self-recording electrometer for observations in the stratosphere. Skylight falling through the 0.001 inch slit at the right casts shadows (diffraction images) of fibers on the photographic film placed just behind a horizontal slit in the recording attachment to the left.

four electrometers sent up this summer. The position of the fibers was recorded by throwing their shadow through a horizontal slit upon a moving photographic film. The film itself was wrapped around a drum of 5 cm diameter, which was attached directly to the mainspring of a 15 jewel watch which made one revolution in $6\frac{2}{3}$ hours. Suitable provision was made to stop the watch after one revolution. In order to insure the continuous running of the watch at the lowest temperatures encountered, namely, $-70°C$, kerosene lubrication was used and in addition a spring having about three times the normal tension was added to the normal spring. Also, the watch chamber was kept thoroughly dry with the aid of a side chamber containing P_2O_5.

The electrometer was hung in the middle of a wire protecting cage about a foot in diameter, so that the shock of hitting the ground with some speed as it was brought down in its parachute need produce no serious injury. The weight of the instrument alone was about 450 grams, and with the protecting basket it amounted to about 550 grams. The total weight carried by the balloon, consisting of electrometer, barograph, and parachute was about 1200 grams. To carry up this load we used sounding balloons $2\frac{1}{2}$ meters in diameter when deflated, made by the Continental Caoutchouc Company of Hanover, Germany. These balloons were inflated to give a free lift of about 1200 grams, and this gave a rate of ascent of approximately 250 meters per minute.

III. THE FLIGHTS

We made the flights in different latitudes because we expected to find latitude effects in the very high levels of the atmosphere. One flight was made at Ellendale, North Dakota, and three more were made at Dallas, Texas. The Ellendale instrument, however, has not been recovered, but the three Dallas flights have all brought a return of the instruments, two of which yielded satisfactory records.

In one of these flights an altitude was reached at which, according to the Weather Bureau's official measurement and report, the barometric pressure had fallen to 16 mm. This compares favorably with Regener's[2] flight of the summer of 1932, since he reports his highest reading as taken at a pressure of 22 mm. Despite our higher altitude, however, we have not used our electrometer readings corresponding to pressures below about 60 mm, for above that point the potential of the fibers had fallen below the value at which in our calibration runs we had found that it was safe to count on saturation. On our graph, therefore, the highest reading plotted is at 61 mm, which corresponds to an altitude of 18 km. Up to that point, however, altogether dependable readings could be obtained.

Fig. 2 shows, in the case of the highest ascent, the actual distance as measured in a microscope between the two traces on the film, made by the two fibers, as a function of the time elapsed since the beginning of the flight, a measurement of fiber-distance being made at time intervals 1.25 minutes apart. An inspection of the points so obtained shows how high was the accuracy in the electrometer readings despite the fact that the lack of contrast on the film makes it unsuitable for reproduction.

[2] Regener, Naturwiss. **20**, 695 (1932).

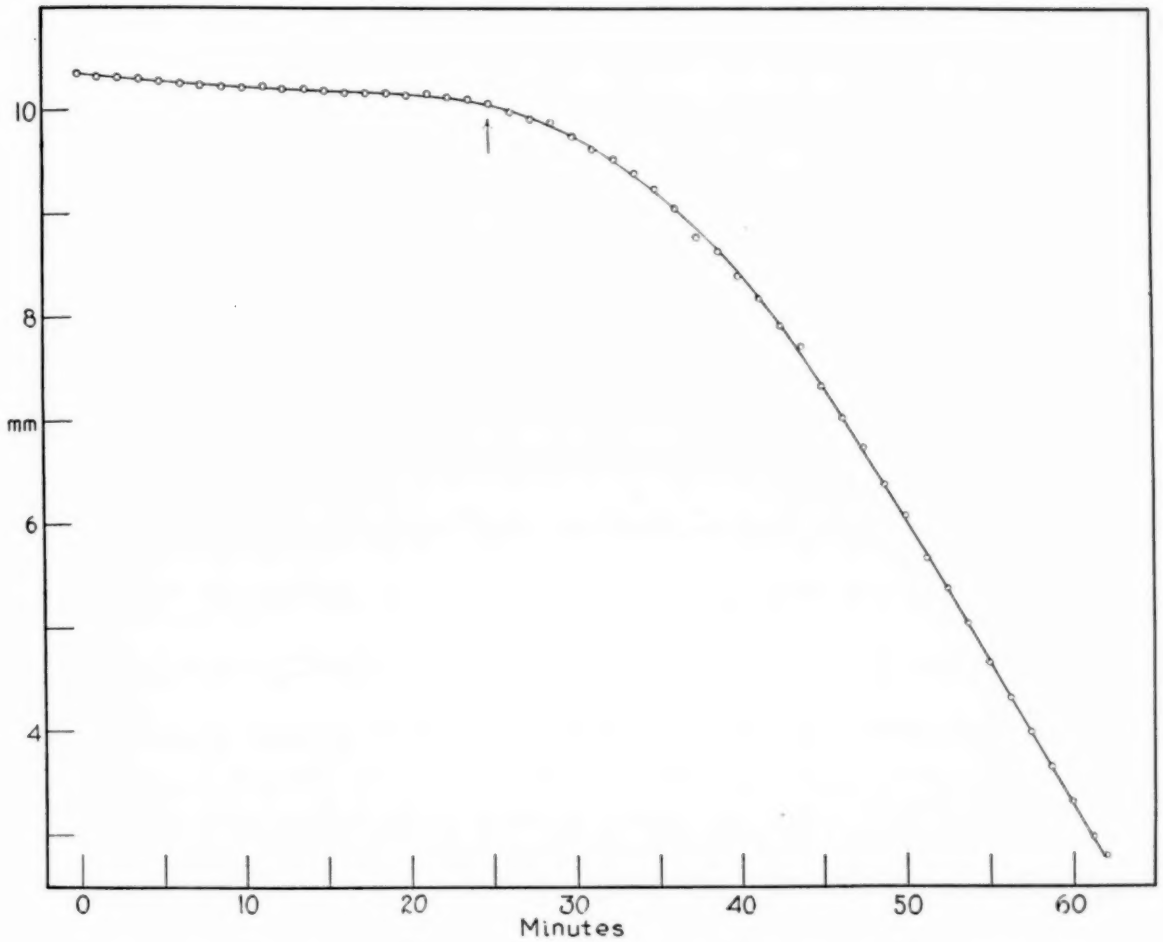

FIG. 2. Separation of traces of electrometer fibers as a function of the time after start of flight.

A second successful flight in which the last electrometer reading corresponded to a pressure of 79 mm (altitude 16.3 km) was also made and yielded a graph which up to that altitude was very nearly as good as that shown in Fig. 2. Our third instrument that came back also had an excellent barometric record which showed that it had reached a pressure of 32 mm (altitude 21.9 km) but the electrometer record was illegible. We succeeded, therefore, in our high altitude summer work of 1932 in obtaining two entirely independent records up to altitudes which correspond respectively to 88 and 93 hundredths of the way to the top of the atmosphere and which, therefore, permit for the first time of a comparison of readings of different instruments and hence of a fairly reliable estimate of the uncertainties actually inherent in this type of observing.

IV. The Treatment of Data

In Fig. 2, as in all work of this sort, the actual readings represent necessarily observed deflections or voltages of the fiber system. To obtain the desired ionization as a function of barometric height it is customary to plot the voltage (or deflection) against time, as in Fig. 2, and then to fit the smoothest possible curve to the average positions of the observed points. The ionization at a given barometer reading is then obtained by taking the slope of this curve corresponding to the barometer reading in question. Following this procedure we have obtained from the smooth curve shown in Fig. 2

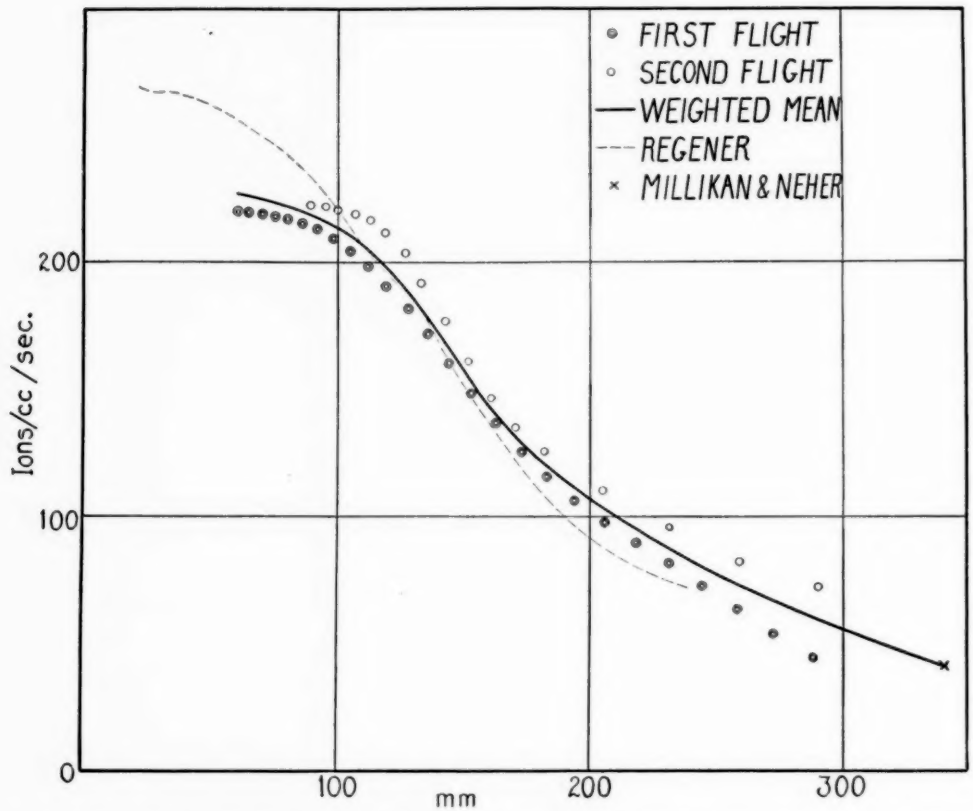

FIG. 3. Ionization per cc per sec. at one atmosphere as a function of barometric height. (Determined from smooth curve in Fig. 2.)

the series of points represented by the double circles in Fig. 3. The curve in Fig. 3 represented by the single circles is obtained precisely similarly from the photographic record of the other successful flight. The heavy curve is the best weighted mean of the two flights which we can make in the light of the whole of our knowledge as to the reliability and consistency of the two sets of readings. Over these curves of ours we have drawn a light dashed curve which represents the results obtained by Regener[2] in his single successful flight of the summer of 1932. The three flights agree well within the limits of uncertainty, which are, in fact, very much larger than the apparent spread of the points for a single flight would seem to indicate.

This matter is of so much importance that we have thought it worth while to devote a paragraph to it, for it is obvious that slopes obtained from such a smoothed out curve as we have considered above give an entirely erroneous idea of the consistency and dependability of the resulting ionizations since the very act of drawing a smooth curve assures the consistency of the differential curve obtained from it and washes out completely the irregularities in the readings. In order to make clear the actual uncertainties involved in the foregoing method of treatment, we have subjected both our own observations and Regener's to the following method of treatment, the results of which we will present in Fig. 4 for flight corresponding to Fig. 2. Instead of drawing a smoothed out curve through the points of Fig. 2, we have determined the ionization by taking the difference of the directly observed voltages of the fibers at intervals of 5 minutes and then dividing the observed voltage-change by the length of this interval. Since the readings plotted in Fig. 2 are taken at intervals of a minute and a quarter, the first point on curve 4 is then obtained from the first and fifth of observed points on curve 2, the

second point on curve 3 from the second and sixth points on curve 2, etc. For the purpose of this plotting the first point on curve 2 which is so used is that marked with an arrow, since for points before this one the ionization is too small to be significantly measured with an instrument whose sensitivity was adjusted for the much larger rates existing at higher altitudes. The spread of the points shown in Fig. 4 will be seen to be quite wide enough to cover the discrepancies between the three curves in Fig. 2. Also, a similar treatment of the data given by Regener and also of the data corresponding to our own second flight, shows an even wider spread of points than that shown in Fig. 4, so

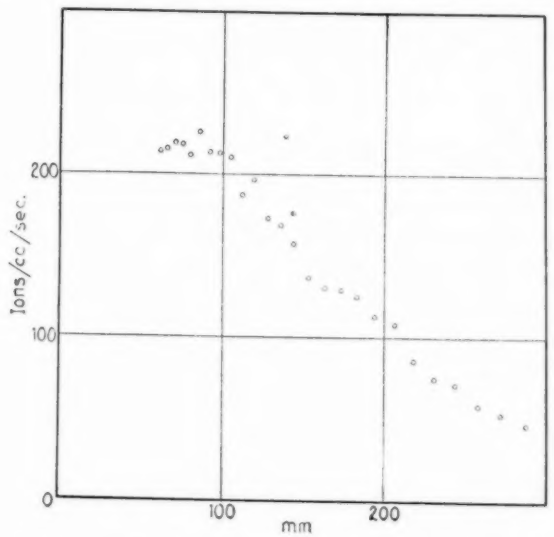

FIG. 4. Ionization per cc per sec. at one atmosphere as a function of barometric height. (Determined directly from points in Fig. 2.)

that there can be no question about the essential agreement found in all the work done with the aid of balloons carrying up self-recording instruments in the summer of 1932.

V. The Discussion of Results

These results are considerably higher at high altitudes than are those which we ourselves obtained in initiating this type of work in 1922.[1] Nevertheless, the only important conclusion which we drew from that first flight still holds (see below). The instruments which we then used were 1/25th as sensitive as those with which the present flights have been made, and we had not at that time succeeded in building instruments whose calibration curves showed an independence of temperature.

The present results are also not in good agreement as to absolute values with those obtained by Piccard[3] in his 1932 manned-balloon flight, for though the shape of his curve is quite like ours his ionization is in general about 40 percent higher than ours, a difference which presumably arises from a difference in the calibration of his capacities. Our own electroscopes were all carefully compared at two different intensities of ionization with the standard electroscope with which Millikan and Cameron[4] have done all their most accurate work. This procedure fixed accurately both the zeros and the capacities of the new electroscopes.

The most significant result which stands out in the curves obtained by all observers in the four high-altitude flights made in the summer of 1932 is that the ionization-altitude curve instead of rising exponentially clear to the top with the value of the apparent absorption coefficient at about 0.6 per meter of water—the value which all observers find between say 5 km and 9 km—shows a marked decrease in this apparent absorption coefficient between 9 km and the top. Indeed, in every one of the four flights, that by Regener, that by Piccard, and the two by ourselves, the ionization-altitude curve above about 12 km actually becomes concave downward instead of remaining strongly concave upward, as, in view of the Gold table, it should do if the coefficient of absorption remained constant. Indeed, the ionization at the highest point reached in these flights would have been twice that observed if the apparent coefficient remained at the value 0.6 per meter of water. Further, if the apparent coefficient is made up of a mixture of rays, as it undoubtedly is, it should have risen even faster. This behavior seems to us completely inconsistent with any theory which (1) makes the incoming rays consist primarily of charged particles of any speeds, or indeed (2) of photons entering the atmosphere in complete equilibrium with their

[3] A. Piccard and M. Cosyns, Comptes Rendus **195**, 604–606 (1932).

[4] R. A. Millikan and G. H. Cameron, Phys. Rev. **37**, 235–252 (1931).

secondaries. It also requires (3) that no rays of penetrating power the same as that of gamma-rays, or of rays intermediate in energy between gamma-rays and the least energetic cosmic rays, can enter the atmosphere in intensities comparable with those of the cosmic rays, for both our own flights and Regener's reach more than 92 percent of the way through the atmosphere and the remaining 8 percent (in Regener's case nearer 3 percent) which is the equivalent of 70 cm of water is insufficient to absorb even the gamma-rays of radium.

In spite of the agreement of all flights by all observers as to the trend of the curve toward a maximum as the top of the atmosphere is approached, caution must still be observed about asserting the correctness of this shape as a reference to Fig. 4 clearly shows. We ourselves regard the chief element of weakness in the accuracy of these curves to inhere not so much in the records of the electrometers as in those of the barographs, for at the very low pressures existing above say 17 km (7 cm of Hg) a small error in millimeters of mercury becomes a large percentage error, and the shape of the curve becomes here very sensitive to such errors. In spite of this caution the definite failure of all the curves to rise sharply as the top is approached to anything like the value required either by a constant absorption coefficient or one increasing in value near the top seems to us to justify the foregoing conclusions as the lack of equilibrium of the entering rays with their secondaries,—the most significant conclusion which we have at any time drawn from our very high altitude work.

The foregoing studies have been made possible, in the first instance, by the Carnegie Corporation of New York, to whom we make grateful acknowledgment for the necessary funds; in the second instance by the U. S. Weather Bureau whose Director, Charles F. Marvin, Assistant Director, Willis R. Gregg, Observer, T. A. Lawler, and other members of its Ellendale, N. D. staff, Meteorologist J. A. Riley and other members of its Dallas, Texas, staff, have rendered very important assistance both in making the flights and in supplying and reading the barographs; and in the third instance by Dr. H. Victor Neher, whose extraordinary skill in making the quartz systems of electroscopes is largely responsible for the excellent performance of these instruments, many of the details of whose mechanical features represent the work, as well as the design, of Mr. Julius Pearson of the Norman Bridge mechanical shop.

A Relation Between Line and Continuous X-Ray Spectra

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It was discovered empirically by Webster that if an electron collides with a silver atom there is a constant ratio between the probability of ejection of a K-electron and the probability of emission of a continuous spectrum quantum of frequency between the critical K-absorption frequency and the high-frequency limit. Webster used voltages from 35 kv to 80 kv. The present work is on palladium and extends the voltage range to 180 kv; the same result holds. A step in the determination of the above ratio is to find the ratio P, for a thick target, of the amount of $K\alpha$ rays resulting from ionization by collision to that resulting from fluorescence. For palladium at normal emergence P is found to be almost constant at 2 up to 180 kv. P is needed in any comparison of the results of thin and thick target line emission experiments since in a truly thin target ionization is by collision only whereas in thick targets fluorescence is also important.

I. THEORY OF THE EXPERIMENT

WE consider here the two principal processes by which an electron passing through an atom can lose a relatively large amount of energy; the ejection of a K-electron and the emission of a quantum of continuous radiation. We consider only continuous spectrum quanta of energy larger than the K-ionization energy and define Q as the ratio of the probability that a bombarding electron will eject a K-electron to the probability that it will radiate a continuous spectrum quantum of frequency greater than the critical K-absorption frequency.

Ideally Q would be determined by plotting from experimental data the spectrum emitted by a very thin target. After dividing all continuous spectrum ordinates by $h\nu$, two graphical integrations would give the desired result. No suitable data are at hand for a single thin target, though data from separate sources for line and continuous spectra are available. Using such data and making assumptions as to the differences between the elements of the spectra from the different elements forming the targets, Webster and Hansen were able to show that over a small voltage range Q is constant although the absolute value could not be obtained.[1]

Considering the great scarcity of thin-target data, however, it would seem that thick target data must do temporarily and it is Webster's thick-target method that is used here.[2] It suffers from the defect inherent in thick-target investigations of those atomic phenomena which depend on the speed of the bombarding electrons: the measured quantity is an integral over all electron velocities and a determination of the integrand must involve differentiation of an empirically determined function and usually also some assumptions about the laws of retardation and diffusion of cathode rays. Thus we first find $\overline{Q}$ an average value of Q from which Q can be calculated.

The general idea of the method is as follows: From measurements on the line radiation from a special composite target and some calculation we find what part of the line radiation results from ionization by collision and what part is due to fluorescence. But the fluorescence rays are a measure of the continuous spectrum intensity and so we are able to calculate the number of continuous spectrum quanta of energy greater than the K-energy and to compare this with the number of K-ionizations resulting from direct impact.

Obviously a quantitative formulation of the method of determining $\overline{Q}$ will be much facilitated by an understanding of exactly how P is found and we therefore digress for a moment to explain this.

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[1] D. L. Webster and W. W. Hansen, Phys. Rev. **33**, 635 (1929).

[2] D. L. Webster, P. N. A. S. **14**, 339 (1928).

A thick target or block of silver is covered with a foil of palladium thick enough to stop all the incident cathode rays. These elements are adjacent in the periodic table so that any small differences between them can be allowed for without difficulty while on the other hand the line radiations have sufficiently different wavelengths to be easily separable. Now all the radiation from the silver block is excited by fluorescence while that from the palladium is excited both by fluorescence and by direct impact of the cathode rays. Fluorescence rays are here called "indirect," rays resulting from ionization by collision are called "direct." Let the following symbols be defined.

P = direct $K\alpha$ line radiation from a thick palladium target/indirect $K\alpha$ line radiation from the same target;

d = direct $K\alpha$ line radiation from palladium foil ($(d+i)$ is measurable);

i = indirect $K\alpha$ line radiation from palladium foil ($(d+i)$ is measurable);

I' = indirect $K\alpha$ line radiation from silver block (measurable);

I = indirect $K\alpha$ line radiation which would come from a palladium block;

$\beta = I/I'$ (calculable);

$\gamma = i/I$ (calculable).

All these quantities are for normal emergence and the intensities are expressed as energy per unit time, per unit solid angle, and per unit current. Then

$$P=\frac{d}{i+I}=\frac{(d+i)-i}{I(\gamma+1)}=\frac{(d+i)-\gamma\beta I'}{\beta I'(\gamma+1)}=\frac{(d+i)/I'-\gamma\beta}{\beta(\gamma+1)}.$$

Now with no further data and only a slight additional calculation $\bar{Q}$ may be obtained. For the quantity $i+I$ can be computed in terms of some empirical expression for the intensity of the continuous spectrum and various absorption coefficients, etc. Multiplying by P, correcting for target absorption, dividing by the fluorescence efficiency and $h\nu_\alpha$, and multiplying by 4π we get the number of direct K-ionizations. With the same assumption about the continuous spectrum as before, an integration gives the number of continuous spectrum quanta produced having frequencies between the short wave limit ν_0 and the K-absorption frequency ν_K. Dividing, one gets $\bar{Q}$, any unknown constant factor for the intensity of the continuous spectrum cancelling out. Thus

$$\bar{Q}=\frac{P(I+i)e^{+\mu_\alpha\bar{x}}}{\nu_\alpha u_\alpha\int_{\nu_K}^{\nu_0}\frac{\boldsymbol{I}(V,\nu)}{\nu}\,d\nu}.$$

Here $\boldsymbol{I}(\nu_0, \nu)$ is the continuous spectrum intensity per unit frequency interval, for voltage V, μ_α is the absorption coefficient of the target for its own α-line radiation, $\bar{x}$ is the mean depth of production of the directly excited line radiation, and u_α is the α-line fluorescence efficiency or fraction of K-ionizations that result in the emission of an α-line quantum.

Knowledge of the quantities β, γ, and $(I+i)$ was presupposed above. To obtain values of these one proceeds as follows. Let I_+ and I_- be the indirect α-line rays produced in a solid palladium target at depths greater than and less than the mean depth of production of the continuous rays. This mean depth is assumed equal to the mean depth of production of directly produced line rays. Then, assuming a form for the continuous spectrum and supposing it to be produced at the depth $\bar{x}$, one can compute I_+, I_-, and I. By subtraction one finds i. I' is obtained from I by correcting for the slight differences between silver and palladium. β, γ and $(I+i)$ are then easily found. The expressions for the three quantities calculated first are[3]

$$I_+ = Re^{-\mu_\alpha\bar{x}}F(V,0),$$
$$I_- = R\Phi(V,\bar{x}),$$
$$I = Re^{-\mu_\alpha x_1}F(V, x_1-\bar{x}),$$

[3] In Webster's paper[2] the factor μ_K/μ was left out. To correct for this his values of Q and N_K should be multiplied by μ_K/μ.

$$F(V,x)=\int_{\nu_K}^{\nu_0}\frac{\boldsymbol{I}(V,\nu)}{\nu}\frac{\mu}{\mu_\alpha}\{e^{\mu_\alpha x}Ei[-(\mu+\mu_\alpha)x]-Ei(-\mu x)\}d\nu,$$

$$\Phi(V,x)=\int_{\nu_K}^{\nu_0}\frac{\boldsymbol{I}(V,\nu)}{\nu}\frac{\mu}{\mu_\alpha}\{e^{-\mu_\alpha x}[Ei(-(\mu-\mu_\alpha)x)-\log|1-\frac{\mu_\alpha}{\mu}|]-Ei(-\mu x)\}d\nu,$$

$$R=\tfrac{1}{2}\mu_\alpha\nu_\alpha(\mu_K/\mu).$$

Quantities not defined previously are, ν_α the alpha-line frequency, x_1 the film thickness, μ the absorption coefficient, μ_K the part of this due to the K-electrons, and μ_α the absorption coefficient at the α-lines.

Before integration is possible, values of the various constants are needed and also some knowledge of the functions $\boldsymbol{I}(V,\nu)$ and $\mu(\nu)$.

For $\boldsymbol{I}(V,\nu)$ Webster used the approximate empirical formula

$$\boldsymbol{I}(V,\nu)=k[(\nu_0-\nu)+B]=k(\nu_0'-\nu).$$

The amount by which ν_0' differs from ν_0 he estimated from isochromats of molybdenum. No such data are available above 100 kv but the lack is not serious for if $k(\nu_0'-\nu)$ is set equal to $k'(\nu_0-\nu)$ at the palladium K-limit the difference between the two forms will be appreciable only where it matters the least, i.e., near the high-frequency limit. Interchange of the two functions will therefore affect any of the functions calculated above only slightly and the ratios β and γ still less, since all the intensities are altered in the same direction. A special calculation showed that using a formula like Webster's would change the values of I_+, I_-, and I by less than five percent in the most extreme cases, and their ratios by much less. We have therefore used the simpler formula in this work.

For μ as a function of frequency we have used Owen's law, taking μ as $(6.13\times10^{27}\ \text{cm}^{-4}\times c^3\nu^3+12\ \text{cm}^{-1})$. The value of μ used was 170 cm^{-1}. The ratio μ_K/μ was taken to be constant at 0.87. These values are obtained from Richtmyer's data[4] on silver.

To determine $\bar{x}$ measurements on the mean depth of production of the continuous radiation from the bare silver block were made. The mean depth of production in the palladium foil was then obtained from this result by multiplying by the ratio of the number of electrons per unit volume in silver to the corresponding number in palladium. The resulting values of $\bar{x}$ are given in Table I. It is seen that the mean depth of pro-

[4] F. K. Richtmyer, Phys. Rev. **27**, 1 (1926).

TABLE I. *Experimentally determined values of* $(d+i)/I'$ *and the resulting values of* P *and* Q.

Kilovolts	40	60	80	100	100	120	140	160	180
Calculated Quantities									
I_+/D	0.146	0.590	1.16	1.78	1.78	2.40	3.02	3.59	4.12
I_-/D	0.025	0.126	0.327	0.65	0.65	1.08	1.52	2.03	2.55
I/D	0.041	0.219	0.499	0.88	0.35	0.56	0.78	1.04	1.41
I'/D	0.039	0.209	0.507	0.91	0.38	0.59	0.84	1.13	1.51
β	1.06	1.05	0.98	0.97	0.92	0.95	0.92	0.92	0.93
γ	3.17	2.27	1.98	1.76	5.94	5.21	4.82	4.40	3.73
$(i+I)/D$	0.171	0.716	1.487	2.43	2.43	3.48	4.54	5.62	6.67
Measured Quantities									
$10^4\bar{x}$ in cm	0.75	1.31	2.13	3.19	3.19	4.49	6.16	8.21	10.9
10^4x_1 in cm	10.1	10.1	10.1	10.1	25.2	25.2	25.2	25.2	25.2
$(d+i)/I'$	12.0	9.15	7.95	7.12	18.7	17.4	15.7	14.3	12.9
Results									
P	1.95	1.98	2.05	2.03	2.07	2.12	2.09	2.06	2.13
Q	0.86	0.83	0.85	0.84	0.86	0.88	0.87	0.85	0.89
$P/(P+1)$	0.66	0.66	0.67	0.67	0.67	0.68	0.68	0.67	0.68

duction increases very rapidly with increasing voltage, especially with the higher potentials. This rapid increase with voltage made necessary the rather thick foils (25.2 microns) at the higher voltages. Measurements of P, when the foil thickness was not at least twice the mean depth of production came out low indicating some direct excitation in the block.

The thickness of the foils was determined both by absorption measurement at the silver α-lines and the weight and area method. The two methods agreed within one percent, indicating that not many holes or thin spots were present in the foil.

After changing the variable ν to $s=\nu/\nu_K$ the above expressions were integrated by Simpson's rule. In the majority of cases sufficient accuracy was obtained by taking ten panels, for the lower voltages six panels sufficed. The exponential integrals were found by interpolation from Glaisher's[5] tables and in special cases, not covered by these tables, by evaluating the significant terms in a series expansion for the exponential integral.

The final results of the calculations are given in Table I. D is equal to $Rk'\nu_K$.

II. Apparatus

The x-ray tube used throughout this work has been described elsewhere.[6] The only alteration has been to install a metal CO_2 trap instead of the glass one described. The tube was completely surrounded by a lead house.

The oil-cooled anode was a block of silver, soldered to a brass base and surrounded by a brass cylinder so constructed as to make the space in the vicinity of the face of the silver block practically field free. The angle of incidence of the electron stream was 30 degrees and the rays were taken out normal to the target face through a window cut in the brass cylinder. The face of the silver block was made into a segment of a cylinder about 5 cm in radius so that the palladium foil could be tightly stretched over the silver. This was accomplished by means of a flat spring device which kept a tangential pull on the foil so that upon heating by cathode-ray bombardment the film would not warp away from the block and allow the primary-continuous rays from the palladium to spread before striking the silver, thereby producing their indirect-characteristic rays outside the region of the target visible through the slit system of the spectrometer.

The palladium foil used for voltages between 40 kv and 100 kv was one layer of foil rolled by Baker and Company to a nominal thickness of 0.004 inch. For voltages between 100 and 180 kv two layers of 0.005 inch foil were used together with a backing of 20 micron aluminum foil. This aluminum foil was put between the palladium and silver to make absolutely certain that direct ionization would not be produced in the silver by cathode rays passing through holes or thin spots in the palladium. A correction for the aluminum foil was included when calculating I' from I. The palladium foils proved to be quite durable standing continuous operation with a power input of six watts.

The spectrometer was of the usual Bragg type for measurement of x-rays by ionization. The x-ray beam was defined by the brass window frame on the tube and the Seeman slit on the calcite crystal. Two other slits, one placed in front of the ionization chamber and one between the crystal and the tube, were used to eliminate any stray radiation. The spectrometer has three unusual features. It is calibrated to read directly in x-units, this being facilitated by the sine-bar method of reading angles. The crystal table is mounted on ball bearings. This type of bearing eliminates all spring in the bearing and insures duplicability of setting. Finally the ionization chamber is really two identical chambers built in one unit. Only one of these is exposed to the x-ray beam and connections are such that the currents due to residual ionization in the two chambers balance out thus eliminating the need for a radioactive compensator.

In measurements of the type included in this research a steady source of high potential direct current is needed. A description of the high-voltage apparatus used will be given elsewhere.[7]

[5] J. W. L. Glaisher, Phil. Trans. (London) **160**, 367 (1870).

[6] W. W. Hansen, Rev. Sci. Inst. **2**, 820 (1931).

[7] D. L. Webster, W. W. Hansen and F. B. Duveneck, Phys. Rev., to be published soon.

III. Data and Results

By using the composite target the Pd $K\alpha$ and the Ag $K\alpha$ lines were carefully located. Several readings were taken on the peak of one; then the spectrometer was set on the other and a number of readings taken there. This process was repeated a number of times for each spectrum resulting in 12 to 15 determinations for the α-line peaks. Several continuous-spectrum points were then taken. The continuous-spectrum ordinates to be subtracted from α-line ordinates were determined by interpolation between the continuous-spectrum points measured. Usually three spectra for each voltage sufficed, as the ratio of the α-line ordinates came out nearly the same within a few percent.

Table I gives the experimentally determined values of $(d+i)/I'$ and the resulting values of P and $\overline{Q}$.

In Fig. 1, P, $\overline{Q}$ and the fraction $P/(P+1)$ are

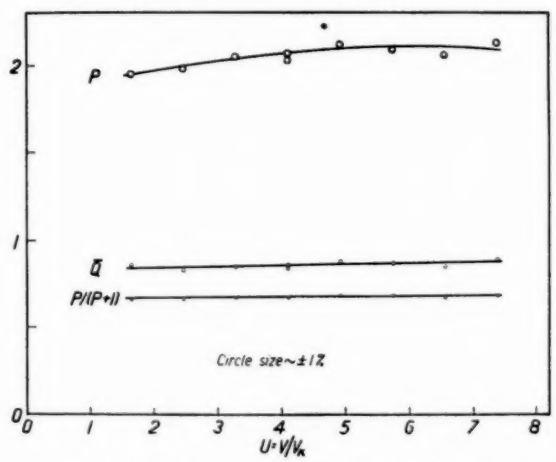

FIG. 1. P, Q and the fraction $P/(P+1)$ are plotted as functions of voltage.

plotted as functions of voltage. This last quantity is of interest in comparing results of thick target experiments with those from thin; it is the fraction of the normally emergent α-line intensity which is directly produced.

It will be observed that $\overline{Q}$ is independent of voltage. It follows that Q is also constant and equal to $\overline{Q}$. The reasoning is, in this rather unusual case, independent of any knowledge of the laws of cathode-ray retardation or diffusion.

As to the important question of the limits of error it is extremely difficult to give a reliable estimate. Judged by the mean deviations of results from various spectra, the random error is about two percent. The consistent error is hard to evaluate because there are several assumptions made in the development of the theory which are certainly not exactly correct. But it is believed that all are as good as can reasonably be obtained and in most cases it will be found that the assumptions are rather better than would appear at first sight. A particular case where the theory is put to a severe test is that in which a rather thick foil is used at low voltages. Here the part of I' due to rays just harder than ν_K is almost entirely lost so that one is calculating a rather small quantity and for the same reason measuring a relatively weak silver line. But actually it is found that experiments with thick and thin foils at 100 kv give almost the same result and this would seem to be a good overall check on the theory. But with so many known possible sources of error, and perhaps some unknown, it is difficult to say exactly what the above-mentioned agreement proves. We believe, however, that the values given for P and $\overline{Q}$ are accurate to within 10 percent. We are unable to give a reliable estimate of the possible limits of error for Q.

The present results confirm Webster's results on silver. On the other hand we cannot understand the conclusion of Wisshak that P varies over quite a range.[8]

IV. Discussion

The apparent constancy of $\overline{Q}$ and hence of Q over a voltage range in which the constituent probabilities vary by a factor of 50 is certainly interesting, if true, and questions immediately arise as to the behavior of Q at lower and higher voltages than those here used.

When the energy of the bombarding electrons is less than or equal to the K-excitation energy Q is of the form zero over zero and a question is: as the voltage across the x-ray tube decreases and approaches the K-excitation voltage, i.e., as $U=\nu_0/\nu_K$ approaches unity, what limit does Q approach? This question is best answered by considering the radiation emitted by a very thin target. As far as the continuous radiation is

[8] F. Wisshak, Ann. d. Physik **5**, 507 (1930).

concerned, it is believed on both theoretical and experimental grounds that the thin-target isochromats are discontinuous at the quantum voltage[9] so that the number of quanta of frequency greater than ν_K rises linearly with $U-1$, the excess of voltage over the excitation voltage. For Q to approach a finite and non-zero limit the number of line quanta emitted must also rise linearly with $U-1$. Experiments soon to be published[7] show that this requirement is met so that Q approaches a limit at $U=1$. The conclusion that Q approaches a finite non-zero constant at $U=1$ may also be reached from thick target data though with considerably less certainty. Here the continuous spectrum isochromat has a finite discontinuity in its first derivative so that the line intensity must have a finite discontinuity in second derivative.

The next question is how is the value approached by Q at $U=1$ related to the value of Q from $U=1.64$ (40 kv) to $U=7.4$? Here again there are two lines of evidence, one from thick target data and the other from thin. For information from thick targets we can take an empirical expression for the continuous spectrum intensity such as that previously used, divide by $h\nu$ and integrate and compare the result with an empiricially determined function for the line intensity. By using the formula $I=K(\nu_0-\nu)$ which corresponds closely to the continuous spectrum intensity after correction for rediffusion[10] and with accurate line intensity data[7] also so corrected it appears that $\overline{Q}$ does not change by more than 25 percent in going from $U=1$ to $U=1.6$. A more reliable estimate of the change in Q over this range can be obtained by comparing data on thin target continuous spectra with independent data on thin target line spectra. This has already been done[1] with the result that Q was found to be practically constant from zero to at least $U=1.6$. This result is somewhat uncertain because Kulenkampff's data were not corrected for diffusion and because in approximating the continuous spectrum of silver on the basis of Kulenkampff's aluminum data it was supposed that the nonlinear term in the thick target continuous spectrum function for heavy elements is due to an essential difference in the thin target spectra whereas actually it seems to be caused by rediffusion.[10] Taking these facts into account, it would seem that Q does not vary more than 50 percent in going from $U=1$ to $U=1.6$. The thick target calculation indicates that Q is less at $U=1$, the thin target that it is greater.

Finally we may speculate as to the behavior of Q at very high voltages. Here we have only theory to guide us. For ease in integration we may take Kramers' theory of the continuous spectrum[11] and so find the number of continuous spectrum quanta between ν_K and ν_0 to be const.$\times(\log U)/U$. This is exactly the form approached at *very* large values of U by Bethe's theory of K-ionization,[12] but much confidence should not be placed in the calculation as Kramers' theory is not the best available one.

In the above calculation such high values of U are needed before Bethe's theory is well represented by the formula given that one feels that relativistic theories should be used. A theory of ionization taking into account relativity effects is known[13] and predicts that at extremely high voltages the probability of ionization passes through a minimum and starts to rise slowly. Does Q then increase at these extreme voltages? We have made a calculation which shows that at very high voltages the continuous spectrum intensity also rises. Though no quantitative predictions as to Q can be made, this calculation shows that it is not impossible for Q to remain constant.

In conclusion, we wish to thank Professor D. L. Webster, under whom the investigation was carried out, for his generous help and advice.

[9] D. L. Webster, Phys. Rev. **9**, 220 (1917); Kulenkampff, Ann. d. Physik; P. A. Ross, unpublished isochromats from a tube with a mercury vapor target.

[10] D. L. Webster, H. Clark and W. W. Hansen, Phys. Rev. **37**, 115 (1931).

[11] H. A. Kramers, Phil. Mag. **46**, 836 (1923).

[12] H. Bethe, Ann. d. Physik **5**, 325 (1930).

[13] C. Moller, Ann. d. Physik **14**, 531 (1932).
H. Bethe, Zeits. f. Physik **76**, 293 (1932).
J. F. Carlson and J. R. Oppenheimer, Phys. Rev. **41**, 763 (1932).

Diffuse Scattering of X-Rays from Sylvine. III. Scattering at the Temperature of Liquid Air

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This paper is an extension of previous work on the diffuse scattering of homogeneous x-rays from sylvine. Measurements have now been carried out at the temperature of liquid air. It is found that taking into account uncertainties in the measurements of both the diffuse scattering and regular reflection the formula $S=(f^2-F^2)/Z+(1-f^2/Z^2)/(1+\alpha \text{ vers } \phi)^3$ probably accounts for the intensity of the scattering within the limits of experimental error for the range of temperature used.

I. INTRODUCTION

IN a recent paper[1] the absolute intensity of x-rays diffusely scattered from sylvine was measured with homogeneous Mo $K\alpha$ radiation obtained by the use of balanced filters.[2] It was found that the f values calculated from these measurements were in good agreement with Wollan's results[3] for argon except at small angles and also with the theoretical values of James and Brindley.[4] It was further found that the use of homogeneous radiation improved the agreement with theory at large angles as compared with the results of previous work with inhomogeneous radiation.[5] Previous results at the temperature of liquid air[6] while in qualitative agreement with theory showed a greater decrease in the scattering than was to be expected. In this work also inhomogeneous radiation was used and the intensities were measured photographically, a combination which makes it practically impossible to correct for the increased absorption of the incoherent scattering and is in general not satisfactory. The measurements here reported have been carried out with homogeneous Mo $K\alpha$ radiation and an ionization chamber.

II. APPARATUS AND PROCEDURE

The apparatus used in this experiment was the same as that used in the measurements at room temperature[1] except it was of course necessary to arrange for cooling the crystal. The cooling chamber used is shown in Fig. 1a. It consisted of an outside brass cylinder A the diameter of which was 3.25 inches. Celluloid windows 0.005 inch thick were provided for the x-rays. The bottom of this cylinder was threaded on the inside to receive a cap B which rested

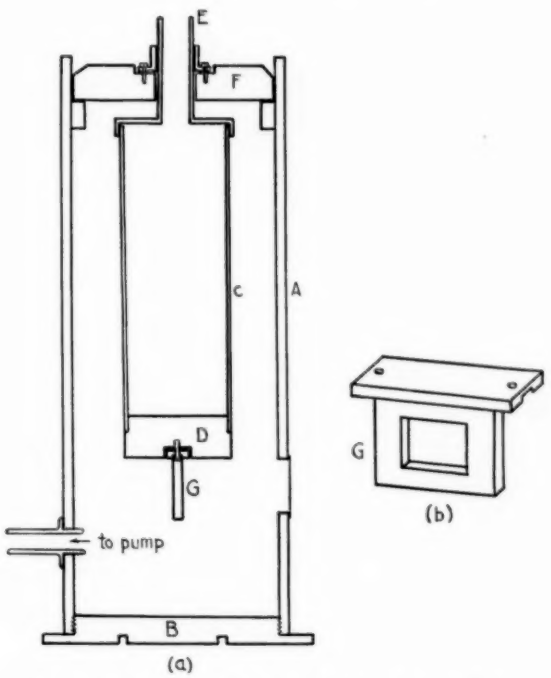

FIG. 1. Cooling chamber and crystal mounting.

* National Research Fellow.

[1] G. G. Harvey, Phys. Rev. **43**, 591 (1933).

[2] P. A. Ross, Phys. Rev. **28**, 425 (1926).

[3] E. O. Wollan, Phys. Rev. **37**, 862 (1931).

[4] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

[5] G. G. Harvey, Phys. Rev. **38**, 593 (1931).

[6] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1925 (1931).

centrally on the crystal table of the spectrometer. The crystal table was provided with two pins which fitted into corresponding holes in B thus enabling the cooling chamber to be removed and replaced in the same position. Concentric with A was a thin brass cylinder C to the bottom of which was soldered a thick copper disk in which there was milled a slot to receive the crystal holder. The top of the cylinder C was reduced in size as shown so that the portion of metal exposed to the outside air should be as small as possible. It passed through a Bakelite cap F which was bolted to a brass ring. The space between A and C was evacuated by means of a Hyvac pump to a pressure of about 0.001 mm of mercury. As the tube passing through F is practically at liquid air temperature it is not possible to use a wax seal. To obtain a tight joint a brass collar was soldered to the tube E and bolted by means of six screws to the Bakelite cap. A rubber gasket well smeared with stopcock grease was found to give a reasonably tight joint even after the grease had frozen. An enlarged view of the crystal mounting G is shown in Fig. 1b. The crystal fitted closely in a recess in the copper mounting and was fastened with a small amount of sealing wax, the crystal being in direct contact with the metal, however. The mounting was bolted in the slot in the copper disk D by means of two screws. This arrangement was used so as to make it possible to change crystals without unsealing any joints except that of the cap B. When in use at low temperature the cylinder C was always kept more than half filled with liquid air although previous test had shown that the crystal temperature was practically that of liquid air so long as any remained in the flask. The chamber worked rather better than was expected requiring about 300 g of liquid air per hour and remaining entirely free from moisture deposits.

The experimental procedure was to measure the ionization current for various values of θ, the angle between the normal to the crystal face and the primary beam of x-rays, at room temperature and immediately after at the temperature of liquid air for a given scattering angle ϕ. The ratio of these two currents for $\theta=\phi/2$ could then be obtained.

III. Results

It has been shown[7, 8] that the intensity of the diffuse scattering from a simple cubic crystal consisting of atoms of one kind should on the classical theory be given by

$$S_{\text{class.}}=1+(Z-1)f^2/Z^2-F^2/Z \qquad (1)$$

with the usual notation. Woo[9] has independently shown that on taking account of the change of wave-length due to the Compton effect the scattering is given not by Eq. (1) but by

$$S=(f^2-F^2)/Z+(1-f^2/Z^2)/(1+\alpha \text{ vers } \phi)^3 \qquad (2)$$

where the first term refers to the coherent and the second to the incoherent part of the scattering. What is actually measured, however, is the ionization current produced by the scattered radiation, or rather the ratio of the ionization currents at the two different temperatures of the crystal. By referring to the paper of Jauncey and Williams[10] it may easily be shown that this ratio is given by

$$\frac{i_1}{i_2}=\frac{f_1^2-F_1^2+(1-f_1^2/Z^2)TZ(K_\phi/K_0)/(1+\alpha \text{ vers } \phi)^3}{f_2^2-F_2^2+(1-f_2^2/Z^2)TZ(K_\phi/K_0)/(1+\alpha \text{ vers } \phi)^3}\equiv\tau, \qquad (3)$$

where K_ϕ/K_0 is the ratio of the absorption in the ionization chamber for a wave-length $\lambda+0.024$ vers ϕ to that for a wave-length λ and the factor T is due to the fact that the modified radiation is more strongly absorbed in the crystal itself. If it is assumed that F is the only quantity in Eq. (3) that is affected by temperature (i.e., $f_1=f_2=f$) then by using values of f obtained at room temperature[1] together with James and Brindley's values[11] of F_1 and F_2 at

[7] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

[8] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931).

[9] Y. H. Woo, Phys. Rev. **38**, 6 (1931).

[10] G. E. M. Jauncey and P. S. Williams, Phys. Rev. **41**, 127 (1932).

[11] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

the temperature of liquid air (86°K) and room temperature (290°K), respectively, we may calculate values of τ, the temperature effect to be expected. The values so calculated are denoted by τ_c in Table I. The experimental values of

TABLE I.

ϕ	$(\sin\phi/2)/\lambda$	τ_c	τ_{exp}	f_1	f_2	F_1	F_1 (J.&B.)
10°	0.123	0.54	0.41	15.05	15.15	14.90	14.80
20°	0.245	0.68	0.61	11.39	11.61	10.78	10.55
30°	0.365	0.68	0.62	8.83	9.03	7.85	7.65
40°	0.482	0.72	0.67	7.58	7.61	6.10	6.00
50°	0.596	0.71	0.70	6.65	6.65	5.10	5.10
60°	0.708	0.72	0.70	5.91	5.95	4.40	4.35
70°	0.804	0.74	0.73	5.50	5.6	3.85	3.70
80°	0.905	0.80	0.79	4.66	4.7	2.94	2.93
90°	0.995	0.85	0.86	4.35	4.3	2.26	2.35
100°	1.080	0.89	0.84	3.57	3.6	2.14	1.90
110°	1.154	0.92	0.90	3.22	3.25	1.59	1.55

i_1/i_2 are denoted by τ_{exp}. It is seen that except at large angles of scattering the experimental ratios are in every case slightly smaller than the calculated values. At large angles the experimental ratio is subject to a larger experimental error since it is the ratio of two small quantities that is involved. In the previous work on this problem[6] the temperature effect for the whole range of scattering angles considered was measured at the same time on the same film so that any extraneous error would be expected to affect all angles in the same sense. In the present case, however, the various points are completely independent which together with the fact that they fall approximately on a smooth curve would seem to indicate that there actually is a slight difference in the values of τ_c and τ_{exp} outside of the limits of experimental error. A possible explanation would be to assume that f is also a function of temperature. F is determined by the electron distribution with respect to a lattice point whereas f depends on the distribution relative to the center of the atom. Since the distance between atoms in a crystal is of the same order as the diameter of the atom it might be thought that at room temperature the available space in which the atom can vibrate is limited whereas at low temperatures the amplitude of the thermal vibrations is smaller (by about 40 percent)[11] and so the atom has "more room in which to be diffuse." This would mean that f might actually decrease with decreasing temperature while, of course, F increases. The effect should only be noticeable at small angles of scattering since it would only be the outer shell of electrons that would be appreciably affected. Such a possibility was suggested some time ago by Professor A. Goetz in a conversation with Professor Jauncey and the writer in connection with previous work on the temperature effect.[6] Assuming the entire difference between τ_c and τ_{exp} at small angles to be due to a change in f we may calculate the change necessary to account for the discrepancy. In Table I the numbers in the fifth column (f_1) are the f values at liquid air temperature so calculated while those in column six (f_2) are the f values at room temperature. It is seen that a very small difference will account for the observed effect.

Another possibility is that the F_1 values at liquid air temperature may be slightly in error at small angles. The correction for extinction becomes important at low temperatures and small angles and is to some extent doubtful. Assuming, then, that f is independent of temperature and taking F_2 at room temperature and τ_{exp} as known we may calculate F values at the temperature of liquid air. The next to last column in Table I shows the values so calculated while the last column gives James and Brindley's results.[11] Here again it is seen that a very small difference will account for the observed effect.

A summary of the results at both room and liquid air temperature is shown in Fig. 2. The solid curves were calculated from James and Brindley's theoretical values[4] of f and experimental values[11] of F at the two temperatures. S_{class} values have been calculated rather than S values so as to give curves which should be independent of the wave-length. The experimental points at room temperature are taken from[1]. In order to obtain S_{class} values at liquid air temperature without making any assumption as to what quantities are affected by temperature the following method was used. It was found that the ratios of the calculated values of S_{class} at liquid air temperature to those at room temperature differ by not more than one percent from τ_c; i.e., the ratios of the ionization currents are equal to the ratios of the S_{class} values to within one percent. Hence the experimental

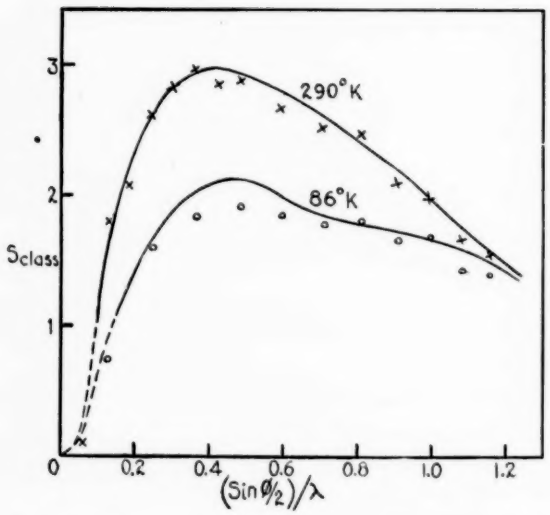

FIG. 2. Summary of the results on the scattering of x-rays from sylvine at both room and liquid air temperatures.

values of S_{class} at room temperature were multiplied by τ_{exp} to obtain S_{class} at the temperature of liquid air. It is seen that at room temperature the experimental points fall on both sides of the calculated curve and probably agree with it within experimental error, while at liquid air temperature the experimental points are predominately on the lower side as pointed out before.

It may not be unnecessary to point out that in calculating such curves one must be very careful to use values of f and F as accurate as possible since it is essentially the difference of the squares of these two quantities that is involved. In fact at small angles $(Z-1)f^2/Z$ is nearly equal to F^2 and as it is necessary to obtain some of these values by interpolation it is essential to use accurate values. It is even then quite possible to obtain values of S differing by one or two percent depending on the error in reading the curves. A possible check is to see that the S values lie on a smooth curve. In view of this it may be that the agreement between the calculated and observed values is nearly as close as can be expected.

III. Conclusion

Measurements of the intensity of the diffuse scattering of homogeneous x-rays from sylvine give values of the atomic structure factor F at the temperature of liquid air which are slightly less than those obtained by James and Brindley from experiments on reflection. The difference, however, is only about one percent and it seems that taking into account the uncertainty of the extinction correction and the experimental error in the intensity measurements in the two cases, the difference is probably explainable without the necessity of introducing any further assumption. As pointed out at the beginning of this paper previous work on the same problem using inhomogeneous radiation gave rather unsatisfactory results. In this connection it is interesting to note that in the case of scattering from CCl_4 and $SiCl_4$ the use of monochromatic radiation has also improved the agreement between the theoretical and observed temperature effect.[12, 13]

In conclusion the author wishes to express his appreciation to Professor Arthur H. Compton for his continued interest and suggestions throughout the course of the work.

[12] R. W. James, Phys. Zeits. **33**, 737 (1932).
[13] W. van der Grinten, Phys. Zeits. **33**, 769 (1932).

The Ultraviolet Absorption Bands of Ammonia[1]

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(Received March 7, 1933)

The ultraviolet absorption bands of ammonia have been investigated in the region from 2400 to 1900A over a wide range of temperatures and pressures. The frequencies of a number of intense double-headed bands have been measured and an analysis of these bands is presented. The doublet separation is nearly constant and is equal to 70 cm^{-1}. Only two fundamental frequencies are observed in the upper state, namely, 890 and 2720 cm^{-1}. The predissociation which occurs in the excited state is discussed and accounted for by assuming that the $\nu_2'(\perp)$ type of vibration of the molecule is always unstable.

Introduction

THE ultraviolet absorption bands of ammonia were investigated by Leifson[3] and shown to consist of a number of diffuse bands extending from 2260A down into the far ultraviolet. Bonhoeffer and Farkas[4] later showed that the ammonia molecule in the excited state does not fluoresce and consequently the diffuse appearance of the bands is not due to unresolved fine structure, but to predissociation. In spite of the difficulties encountered in obtaining a satisfactory analysis for the vibration bands of a polyatomic molecule, it seemed of value to investigate these ultraviolet ammonia bands more carefully than heretofore in order to see if an analysis was possible. The numerous recent investigations of the infrared spectrum of ammonia and the apparent simplicity of the bands reported by Leifson at least made the problem more attractive than would have been the case otherwise. It was obvious that the measurements of Leifson were not accurate, since he stated that only the midpoints of the bands were measured and some later work by Bates and Taylor[5] had shown that the bands possessed a double head between the ends of the bands. In the discussion that follows the cause of the predissociation is considered and an explanation of the phenomenon is given. This matter is of interest in connection with the photochemical decomposition of ammonia.

Experimental

The system necessary for carrying out the experiments consisted mainly of a trap, mercury manometer, absorption cell, suitable connecting tubing and stopcocks. An oil pump served to evacuate the apparatus. One absorption cell was all-quartz, ten inches long, with sealed-on plane ends. The second cell was two inches long, the quartz ends being cemented on with De Khotinsky cement. The longer of the two cells was used to make measurements on the heated gas, hence contained an inset tube at its middle to hold a thermocouple junction. The cell was wrapped with nichrome heating wire and well insulated with asbestos. Ammonia was secured from a small tank, in which it was stored over metallic sodium. The gas was admitted to apparatus as needed, frozen by a solid carbon dioxide alcohol mixture, pumped frequently and then admitted to the absorption cell without further purification.

The hydrogen discharge tube used as a source of light was similar to one described by Bay and Steiner[6] and ran on a current of 300 milliamperes at 8000 volts. Lenses before and after the absorption cell focussed the light on the slit of the spectrograph. Photographs were taken with a Schmidt and Haensch Universal Spectrograph,

[1] Contribution from The Sterling Chemistry Laboratory, Yale University.

[2] Sterling Research Fellow in Chemistry.

[3] Leifson, Astrophys. J. **63**, 73 (1926).

[4] Bonhoeffer and Farkas, Zeits. f. physik. Chemie **124**, 337 (1927).

[5] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

[6] Bay and Steiner, Zeits. f. Physik **59**, 48 (1929).

with one quartz prism. The dispersion was better than 4A per millimeter at 2200A. Below 2000A a Hilger E31 Spectrograph was employed, the dispersion amounting to about 11A per millimeter. The slit width used was 0.02 to 0.03 mm and the time of exposure usually amounted to less than fifteen minutes. An iron arc or aluminum spark served to give a comparison spectrum, the particular standard depending on the wave-length region under investigation. Eastman 33 Plates, with or without Eastman Ultraviolet Sensitizer, were used.

The spectrograms of the ammonia bands were measured on a small Leiss Comparator, which gave the position of any line with an accuracy of about 0.03 mm. The accuracy of the measurements was limited not so much by the accuracy of the instruments used as by the diffuseness of the bands. One or two plates were obtained on which the dispersion was 1A per millimeter and in these cases the bands were so diffuse that it was not possible to measure the plates. At the lower dispersion it was often necessary to mark the positions of the satellite bands (see below) before measuring the plate. The positions of the strong bands were determined with an accuracy of ± 10 cm^{-1}; where the middle of the band had to be estimated the accuracy was only 30 cm^{-1}. It was necessary to vary the ammonia pressure by relatively small increments in order to bring out all of the weak absorption bands recorded below.

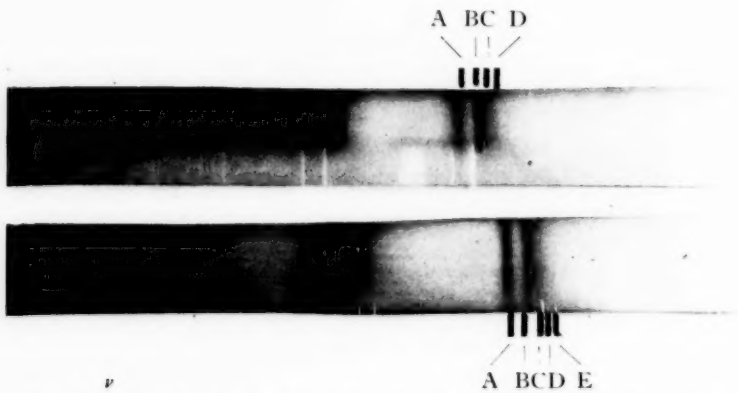

FIG. 1. The ultraviolet absorption bands of ammonia. The principal bands, *A* and *B*, and the satellite bands, *C*, *D*, *E* are marked for the regions near 45,250 and 47,060 cm^{-1}.

RESULTS

Sixteen strong ammonia bands were observed in the region from 1900 to 2400A when the temperature was varied from 25° to 600°C and the ammonia pressure from less than 0.5 mm to 2.5 atmospheres. Each of these bands is doubled and very intense as may be noted in the reproductions shown in Fig. 1. Enough plates were obtained to determine the wave-length of each band from one or more plates and the results are usually the average of measurements on four or more photographs, the greatest weight being placed on those in which the absorption was small. The wave-lengths which were found do not agree with those of Leifson and always correspond to a shorter wave-length. The reason for this is evident, because Leifson measured the center of the absorption band and this point is always to the long wave-length side of the double head. The absorption was greatest at or near the long wave side of the blue component of the doublet and at the short wave side of the red component. These positions of maximum absorption have been measured and called the heads of the band and are denoted by $\tilde{\nu}$ *A* and *B*, respectively, in Fig. 1. As the pressure increased, absorption by the red component increased rapidly towards longer wave-lengths, the blue component spread to the short wave-length side only slightly and absorption between the two heads increased until it was complete. On the long wave-length side of each red component

were certain well-defined absorption maxima, which were observed clearly upon careful regulation of the ammonia pressure. Several of these are indicated in Fig. 1 by *C*, *D*, *E* and *F*. In order to illustrate these absorption maxima, a microphotometer trace of one of the bands is shown in Fig. 2. For the sake of simplicity the intense bands *A* and *B* are called the principal bands and the weak bands *C*, *D*, etc., satellite bands.

In Table I are given the frequencies of the bands measured. The principal and satellite

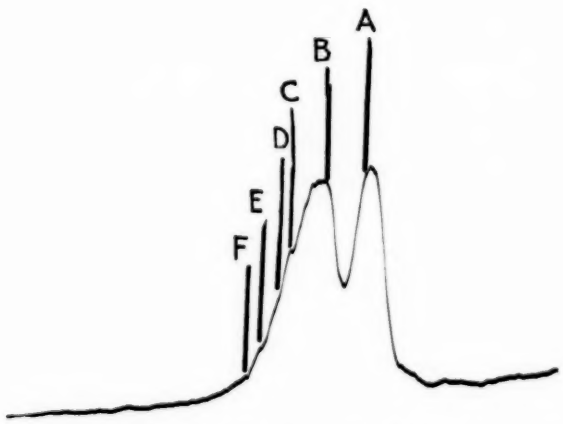

FIG. 2. Microphotometer trace showing the ammonia absorption band at 2124A. *A* and *B* are the principal bands; *C*–*F* the week satellite bands.

bands have been recorded in separate parts of the table, the frequencies in wave numbers are on a vacuum basis and the effect of heat has been noted. The frequency 48,890 cm^{-1} represents the midpoint between the heads of the band and all other measurements at shorter wave-lengths are the midpoints between the ends of the bands. The double-headed bands at 46,140 and 47,030 cm^{-1} are interesting because, upon heating to 150° or 300°C, each of these bands shifted to the red and became in appearance triple-headed. In fact the original double-headed band was present, less intense, however, and a new double-head was present nearby on the long wave-length side. The band at 41,825–41,890 cm^{-1} is less intense than the one to the red and to the violet under the same conditions of temperature and pressure. The frequencies of the satellite branches at approximately 46,900 and 47,800 cm^{-1} are the average of several measurements which agreed well among themselves and consequently considerable confidence can be placed in the results. In nearly all cases the satellite bands occur in pairs, as shown in Table I.

TABLE I. *Ultraviolet absorption bands of ammonia.* (A plus sign in parenthesis after the frequency indicates that an increase in temperature increased the intensity of the band in question.)

cm^{-1}	Assignment	cm^{-1}	Assignment
	A. Principal Ammonia Bands		
41140 (+) 41220 (+)	$\nu_4''\rightarrow\nu_1'(0)$	46140 46200	(origin) $\nu_1''(0)\rightarrow\nu_1'(0)$
41825 (+) 41890 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_1'(0)$	46980 (+) 47060 (+)	$\nu_1''\rightarrow 2\nu_1'$
42680 (+) 42760 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_1'$	47030 47090	$\nu_1''(0)\rightarrow\nu_1'$
42810 (+) 42890 (+)	$\nu_3''\rightarrow\nu_1'(0)$	47925 47975	$\nu_1''(0)\rightarrow 2\nu_1'$
43760 (+) 43830 (+)	$\nu_1''+\nu_2''\rightarrow\nu_1'(0)$	48890	$\nu_1''(0)\rightarrow\nu_3'$
		49790	$\nu_1''(0)\rightarrow\nu_1'+\nu_3'$
44540 (+) 44610 (+)	$\nu_2''\rightarrow\nu_1'(0)$	50675	$\nu_1''(0)\rightarrow 2\nu_1'+\nu_2'$
45220 (+) 45280 (+)	$\nu_1''\rightarrow\nu_1'(0)$	51600	$\nu_1''(0)\rightarrow 2\nu_3'$
		52470	$\nu_1''(0)\rightarrow\nu_1'+2\nu_4'$
46040 (+) 46120 (+)	$\nu_1''\rightarrow\nu_1'$		
	B. Satellite Ammonia Bands		
42590	$\nu_1''+2\nu_2''\rightarrow\nu_1'$	46020 46080	
43560 (+) 43640 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_3'$	46875 46910	
43660 (+) 43710 (+)	$\nu_1''+\nu_2''\rightarrow\nu_1'(0)$	46940 46990	
44445 (+) 44500 (+)	$\nu_2''\rightarrow\nu_1'(0)$	47730 47780 47815	
45100 (+) 45160 (+)	$2\nu_1''\rightarrow\nu_1'$	47860	

DISCUSSION

It is apparent that the principal bands consist of a series of double-headed bands, the average separation of the components remaining practically constant and equal to about 70 cm^{-1}. It can be assumed that the doubling is caused by an electronic doublet in the excited state of the molecule. The component bands of such a doublet should be very similar in structure, but,

since it is observed that one component shades to the red and the other to the violet, the explanation is probably incorrect. Furthermore, ammonia possesses an even number of extra-nuclear electrons and hence the multiplicity should be odd and not even. The doubling of the infrared bands of ammonia at 10μ and 3μ has been observed and Dennison[7] has shown that these phenomena are due to the symmetry properties of the ammonia molecule, one form being symmetrical and the other antisymmetrical with regard to their wave functions. The components of the infrared bands are then exactly the same except for a small constant frequency difference between the rotational lines of the same quantum number. Dennison and Hardy[8] pointed out that the frequency difference should become greater for higher vibrational quantum numbers. If an analogous line of reasoning is followed in connection with the electronic bands, it is seen that the facts do not agree with the expectations, since the doublet separation remains constant and the components are not similar in appearance. The best explanation of the doubling is one in which each band is assumed to consist of a P and an R branch, the latter doubling back to the red. This explains why the absorption in the short wave component spread to the violet only slightly and the fact that the absorption in the other component increased rapidly to the red as the ammonia pressure was increased. At high pressures and temperatures the R branch was developed at higher rotational quantum numbers and hence absorbed completely in between the origins of the two branches. Even though the rotational structure is diffuse as a result of predissociation, the effects produced by the branches should be the same as in the case of discrete states. The reason for the large separation of the origins of the P and R branches is not apparent and this difficulty constitutes an objection to the explanation of the doubling.

For the reasons given below the origin of the electronic system is chosen as 46,140 cm^{-1} for the P branch and 46,200 cm^{-1} for the R branch. The subsequent discussion of the analysis of the vibration bands is limited to a discussion of the origins of the P branches, since the origin of each R branch is displaced 70 cm^{-1} from the origin of the corresponding P branch. The intensity of the 46,140 cm^{-1} band decreased and all bands to the red were increased in intensity upon heating the ammonia. This is an indication that the former is located at or to the short wave-length side of the origin. Furthermore, the bands at 45,220 and 44,540 cm^{-1} are separated from the origin by 920 and 1600 cm^{-1}, respectively, and represent transitions from the first two vibrational levels in the lower state to the ground level in the excited state. Infrared data[9] give these frequencies as 933 and 1630 cm^{-1}. No other choice of an origin gives an agreement as satisfactory as the above nor explains the heating experiments and intensities of the bands as well. Bearing in mind that the first two vibration levels observed in the upper state lie 895 and 1785 cm^{-1} above the zero level, the bands to the red of the origin are given the assignments shown in Table I.

The analysis is satisfactory except with regard to several bands. The transition $\nu_1''+\nu_2''\rightarrow\nu_1'(0)$ should be displaced 2500 cm^{-1} from the origin, while the observed value is only 2380 cm^{-1}. Robertson and Fox[10] gave 2500 cm^{-1} as the infrared frequency because it represented the position of maximum absorption in the band, but the absorption at 2380 cm^{-1} was also considerable. The fact that the band results from a combination of a perpendicular and a parallel vibration of the molecule shows that the band is complex and hence it is not possible to predict from which level in the ground state will arise the strongest transition to the upper electronic state. The assignment $\nu_1''+\nu_2''\rightarrow\nu_1'(0)$ to the band at 43,760 cm^{-1} is probably correct for this reason. The satellite branches at 43,660 and 43,710 cm^{-1} are then associated with the same transition, but a smaller probability of transition. The same kind of difficulty arises in connection with the bands at 41,140 and 41,825 cm^{-1}. In each case the observed displacement from the origin is less than the infrared frequency and, as before, the infrared frequency represents the position of maximum absorption. For example,

[7] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[8] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).

[9] Weizel, Handbuch der Experimental Physik; **1**, p. 416 (1931).

[10] Robertson and Fox, Proc. Roy. Soc. (London) **A120**, 161 (1928).

Robertson and Fox[10] give three strong absorption maxima in the infrared at 4504, 4420 and 4320 cm^{-1}, the second of which is slightly stronger than the other two. The band at 41,825 cm^{-1} is displaced from the origin by 4315 cm^{-1}, which agrees with the smallest of the three infrared frequencies but not the other two. Further investigation of the infrared bands may make it clear as to which levels in the ground state are favored as initial states in the electronic bands.

The frequencies in the excited state which are necessary to account for the bands to the short wave-length side of the origin are 890 and 2720 cm^{-1}. The assignments are given in Table I. The wave number differences between successive bands alternates between about 890 and 920 cm^{-1} and hence it is necessary to have two frequencies in order to account for the observed results. Leifson's data show irregularities in the differences which are similar to those observed here. The satellite bands to the short wave side of the origin may arise from the same transitions assigned to the nearby principal bands, but in view of the uncertainty the assignments have not been given in Table I. The bands in the excited state show little, if any, convergence, hence an approximation of the heat of dissociation is not possible.

The fact that only two frequencies appear in the excited state is significant and suggests that one, and possibly two, of the types of vibration in the upper state are unstable. If one considers the mechanical picture of the possible types of vibration of the ammonia molecule,[7] it is seen that the ν_2' vibration should be least stable. This consists of a vibration of the nitrogen atom perpendicular to the axis of symmetry and the oscillation of two of the hydrogen atoms in a direction opposite but parallel to that of the third hydrogen atom. Recent studies of the photochemical decomposition of ammonia and related problems,[11] give a mechanism for the decomposition which requires a primary dissociation into NH_2 and H after the absorption of light. The ν_2' frequency accounts for this dissociation, since one of the hydrogen atoms is unique and dissociation should yield NH_2 and H. Since the frequencies in excited states are usually less than those in the ground states, the frequencies 890 and 2720 cm^{-1} correspond to ν_1'' and ν_3'', respectively, of the ground state. Predissociation is then of the type which is called vibrational predissociation by Herzberg.[12] The energy present in ν_1', ν_3' or a combination of these two passes into the vibration ν_2' and dissociation follows, since the latter is assumed to be unstable. This transfer of energy from one type of vibration to another is assumed to take place in many molecules as will be seen from a perusal of the recent literature on the subject of unimolecular chemical reactions. The type of predissociation suggested for the ammonia molecule accounts for the observation that the absorption bands are diffuse over the entire region investigated.

It is a pleasure to acknowledge and thank Professor W. W. Watson of the Physics Department for his constant interest and help during the course of this investigation.

[11] Wiig and Kistiakowsky, J. Am. Chem. Soc. **54**, 1806 (1932); Dixon, ibid. **54**, 4262 (1932).

[12] Herzberg, Ergebn. d. exakt. Naturwiss. **10**, 207 (1931).

The Infrared Spectrum of Carbon Dioxide. Part I

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Previous work by Fermi and by Dennison has shown that the principal features of the infrared and Raman spectra of carbon dioxide may be explained by taking account of the first order perturbation terms in the potential energy expression. It was not possible to predict the positions of the levels with any high degree of accuracy, however. The present paper extends this work by introducing a second order perturbation. The formula for the second order energy correction of a general linear symmetrical triatomic molecule is initially computed. This formula is then modified in order that it may be applicable to the carbon dioxide molecule in which resonance degeneracy plays an essential rôle. A review is made of the experimental data which determine the positions of the carbon dioxide vibrational energy levels. These include the results of a recent investigation of absorption bands appearing in the spectrum of Venus, as well as new and as yet unpublished data found by Barker and Wu. In all, twenty levels have been found and out of these, eleven are required to determine the anharmonic constants of the molecule. The remaining nine levels may then be predicted, and their positions are found to agree very accurately with the values obtained experimentally. A table is given showing the positions of a number of CO_2 infrared bands which while accessible to observation have not as yet been reported. The recent work by Langseth and Nielsen on the Raman spectrum of CO_2 is discussed.

INTRODUCTION

IT is now well known that the molecule of carbon dioxide possesses a form which is both linear and symmetrical, the carbon atom lying midway between the two oxygens. The group of normal vibrations of such a system constitute a zeroth order approximate solution to the motion which very satisfactorily explains the general features of the infrared spectrum of the molecule. The respective modes of vibration of the three independent frequencies are indicated schematically in Fig. 1.

FIG. 1.

The first of these ω_1 corresponds to a symmetrical motion of the oxygen atoms, the carbon atom remaining fixed at the center of mass. This frequency is inactive in the infrared, but will appear strongly in the Raman spectrum and lies at about 7.5μ. In the second frequency ω_2 the carbon oscillates perpendicularly to the line joining the oxygen atoms, while the distance between the oxygens remains unchanged. ω_2 is a double frequency, active in the infrared, inactive in the Raman spectrum and lies at about 15μ. The unsymmetrical vibration with frequency ω_3 is a motion of the atoms along the figure axis of the molecule in which the carbon moves relative to the center of mass of the oxygens; where again the distance between the latter remains unaltered during the motion. This frequency which is active in the infrared and inactive in the Raman spectrum lies at about 4.7μ.

As has been remarked above, this model fully explains the principal observed features of the spectrum. When, however, the infrared and Raman spectra are examined more carefully, certain details appear which cannot be so simply understood. The Raman spectrum, for example, consists not of one line but of two lines of about equal intensity in the region of 7.5μ. Moreover, many of the combination bands in the infrared deviate from the positions predicted by combination relations by rather large amounts (i.e., approximately 100 waves per cm).

These difficulties have been completely explained by a theory proposed by Fermi[1] and

[1] E. Fermi, Zeits. f. Physik **71**, 250 (1931).

somewhat amplified by Dennison.[2] The explanation depends upon the fact that in carbon dioxide the frequency ω_1 is almost exactly equal to $2\omega_2$. The degeneracy thus introduced produces a first order perturbation which on the one hand changes the identity of the levels, allowing two Raman lines rather than one to appear. On the other hand, the perturbation yields a first order correction to the energy (of the order of 100 waves per centimeter) which accounts for the positions of the combination bands.

The infrared and Raman spectra of the carbon dioxide molecule are known with great accuracy, the errors in the positions of the bands being in the neighborhood of 1 or 2 waves per centimeter. The positions of the combination bands predicted by Fermi's theory fail to agree with the observed positions by amounts of the order of 10 to 20 waves per centimeter. Clearly, these discrepancies must be due to the second order corrections to the energy of which no account was taken in Fermi's theory. It is the purpose of the present paper to introduce this second order correction, and to show that with its aid the positions of the observed lines may be predicted with an error no greater than the experimental one. This procedure will allow a determination of the anharmonic force constants which will prove to be of great importance in determining the general form of the potential function of the carbon dioxide molecule.

Analysis

In presenting the analysis we shall use the coordinates q, z, r and φ which were first introduced and fully described by Dennison[3] in the discussion of the molecule YX_2. q measures the relative separation of the oxygen atoms, z the displacement of the carbon atom from the center of mass of the oxygens measured parallel to the line of the latter, while r and φ are the polar coordinates of the carbon in a plane at right angles to the line of the oxygens, the origin of coordinates lying at the intersection.

It proves convenient to introduce the dimensionless variables σ, ξ, ρ and φ instead of q, z, r and φ which are related to them in the following manner:

$$\sigma=2\pi[\omega_1 m/2h]^{\frac{1}{2}}q, \qquad \xi=2\pi[\omega_3\mu/h]^{\frac{1}{2}}z,$$
$$\rho=2\pi[\omega_2\mu/h]^{\frac{1}{2}}r, \qquad \varphi=\varphi.$$

The Hamiltonian representing the vibrational motion may be readily obtained.[4] The symmetry of the molecule conditions that the Hamiltonian must be an even function of z and r and independent of φ.[5]

In accordance with the series of approximations to be made on the system, the Hamiltonian may be expanded in a power series in λ, a parameter of smallness.

$$H=H_0+\lambda H_1+\lambda^2 H_2.$$

These functions may be quite readily obtained:

$$H_0\equiv(2\pi^2/h)\{2\omega_2 p_\sigma^2+\omega_3 p_\xi^2+\omega_2 p_\rho^2+(\omega_2/\rho^2)p_\varphi^2\}+(h/2)\{2\omega_2\sigma^2+\omega_2\rho^2+\omega_3\xi^2\},$$
$$\lambda H_1\equiv(2\pi^2\Delta/h)p_\sigma^2+h\{(\Delta/2)\sigma^2+a\sigma^3+b\sigma\rho^2+c\sigma\xi^2\},$$
$$\lambda^2 H_2\equiv(\omega_3/2\omega_2 I)\rho^2 p_\xi^2+h\{d\sigma^4+e\rho^4+f\xi^4+g\sigma^2\rho^2+h\sigma^2\xi^2+i\rho^2\xi^2\}.$$

The first order perturbing energy λH_1 contains two classes of terms. The first class represents the fact that ω_1 is not exactly equal to $2\omega_2$, and is proportional to the quantity $\Delta=\omega_1-2\omega_2$. In addition to these terms comes the contribution from the anharmonic potential; namely, all those terms cubic in the coordinates which fulfill the necessary symmetry conditions.

The second order energy may likewise be divided into two parts, the first of which

[2] D. M. Dennison, Phys. Rev. **41**, 304 (1932).

[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[4] A general treatment of the carbon dioxide molecule would involve the use of a Hamiltonian containing rotational coordinates in addition to the vibrational coordinates. Such a treatment would allow us to obtain not only the rotational energy, but also the interaction between rotation and vibration. This problem will be reported in a later paper; for the present we restrict ourselves to predicting the centers of the absorption bands.

[5] Actually the symmetry of the system demands merely that H shall be an even function of z and independent of φ. The fact that we take H to be an even function of r also implies that we assume that H is analytic.

$([\omega_3/2\omega_2 I]\rho^2 p_\xi^2)$ embodies the circumstance that for finite amplitudes of vibration, the molecule deviates slightly from strict linearity. The second part contains the quartic terms of the anharmonic potential of vibration. The solution of the system in zeroth and first approximations has been described in detail elsewhere,[2] and for our present purpose it will suffice to add only a few points to the results already obtained.

The solution of the zeroth order wave equation may be written in the form

$$\Psi_{nt}=\Psi_{(\sigma)}{}^{V_1}\Psi_{(\xi)}{}^{V_3}R_{(\rho)}{}^{V_2 l}e^{\pm il\varphi}.$$

$\Psi_{(\sigma)}{}^{V_1}$ and $\Psi_{(\xi)}{}^{V_3}$ are the well-known Hermitian orthogonal functions with the arguments σ and ξ, respectively. The remaining part $R_{(\rho)}{}^{V_2 l}e^{\pm il\varphi}$ has been described as a two-dimensional Hermitian orthogonal function expressed in polar coordinates.[3] Since various matrix elements of powers of the coordinates will be required, it will be advantageous to examine this expression in greater detail. It may be shown that the differential equation defining it; namely,

$$\{\partial^2/\partial\rho^2+(1/\rho)(\partial/\partial\rho)+(1/\rho^2)(\partial^2/\partial\varphi^2)+[(2E/h\omega_2)-\rho^2]\}\Psi_{\rho\varphi}=0$$

is satisfied by the function (here given in normalized form)

$$R_{(\rho)}{}^{V_2 l}e^{\pm il\varphi}=(k!)^{\frac{1}{2}}\{(l+k)!\}^{-\frac{1}{2}}\pi^{-\frac{1}{2}}\rho^l e^{-\rho^2/2}L_{l+k}{}^l(\rho^2)e^{\pm il\varphi},$$

where $k=(V_2-l)/2$. $L_{l+k}{}^l(\rho^2)$ is the associated Laguerre polynomial of argument ρ^2, from whose properties it will be comparatively easy to evaluate the necessary matrix elements.

The zeroth order energy constant $W_0{}^n$ depends only upon the quantum numbers $2V_1+V_2$ and V_3, thus showing that in this order of approximation the system is degenerate with respect to the quantum numbers V_1, V_2, l. We shall let n represent the former ones and t the additional quantum numbers necessary to define the wave function Ψ_{nt}.

The first order energy constant $W_1{}^{nt}$ is got by equating the secular determinant $|(H_1)_{nt}{}^{nt''}-W_1\delta_{t'}{}^{t''}|$ to zero and solving for the roots w_1. $W_1{}^{nr}$ depends upon the quantum numbers V_1, V_2, V_3, and upon l^2. It is thus independent of the algebraic sign of $\pm l$. This last degeneration is not removed even by the perturbing potential $\lambda^2 H_2$, for $\lambda^2 H_2$ is not a function of the coordinate φ. The appropriate stabilized wave functions for the new levels produced by the first order perturbation are the properly chosen linear combinations $\Psi_{nr}=\sum_t C_{rt}\Psi_{nt}$, where the C_{rt} are given by the first minors of the secular determinant for $W_1{}^{nr}$.

The second order correction to the energy is now determinable in the usual way; that is,

$$W_2{}^{nr}=(H_2)_{nr}{}^{nr}+\sum_{n't'}{}'\{(H_1)_{nr}{}^{n't'}\}^2/\{W_0{}^n-W_0{}^{n'}\},$$

where the dash on the summation sign indicates the omission of those terms for which $n'=n$. This may be expanded into the form:

$$W_2{}^{nr}=\sum_i C_{ri}{}^2[(H_2)_{nt_i}{}^{nt_i}+\sum_{n't'}{}'\{(H_1)_{nt_i}{}^{n't'}\}^2/\{W_0{}^n-W_0{}^{n'}\}]+$$
$$+\sum_i\sum_j C_{ri}C_{rj}[(H_2)_{nt_i}{}^{nt_j}+\sum{}'\{(H_1)_{nt_i}{}^{n't'}\}\{(H_1)_{n't'}{}^{nt_j}\}/\{W_0{}^n-W_0{}^{n'}\}],$$

where the t_1, t_2, etc., are the several sets of the degenerate quantum numbers which identify the members of the stabilized wave function. In the case of a triatomic, linear, symmetrical molecule which is not subject to resonance degeneracy, the second order energy constant is given by

$$W_2{}^{nt}=(H_2)_{nt}{}^{nt}+\sum_{n't'}{}'\{(H_1)_{nt}{}^{n't'}\}^2/\{W_0{}^n-W_0{}^{n'}\}.$$

Unlike the resonance case, in which n comprises $2V_1+V_2$ and V_3, n here refers to V_1, V_2, and V_3 as separate entities. The sum in $W_2{}^{nt}$ is somewhat richer in terms than the corresponding sum

$$\sum_{n't'}{}'\{(H_1)_{nt_i}{}^{n't'}\}^2/\{W_0{}^n-W_0{}^{n'}\}$$

in $W_2{}^{nr}$ because of the absence of the resonance phenomenon. Apart from this difference (which proves to be unimportant), it appears that the second order energy constant for the carbon

dioxide molecule may be expressed as a sum of second order energy constants for the nonresonant type of molecule multiplied by the quantities $C_{\tau t_i}^2$, plus terms which cannot be treated in this fashion and which may be called cross products. A very considerable simplification would be effected in the systematics of the problem if it could be shown that the cross products vanish. For, W_2^{nt} modified by the deletion of terms required by the resonance degeneracy is a definite quadratic function of the quantum numbers; namely,

$$h\{x_0+x_1V_1+x_2V_2+x_3V_3+x_{11}V_1^2+x_{22}V_2^2+x_{33}V_3^2 +x_{ll}l^2+x_{12}V_1V_2+x_{13}V_1V_3+x_{23}V_2V_3\},$$

where the coefficients are known functions of the true anharmonic constants (a, b, c, d, e, f, g, h and i), the fundamental frequencies (ω_1, ω_2, ω_3), and the moment of inertia I, and will be enumerated at a later point in the paper. It would thus be possible to write:

$$\widetilde{\lambda^2W_2^{n\tau}}=h\sum_i C_{\tau t_i}^2\{x_0+x_1V_1+x_2V_2+x_3V_3+x_{11}V_1^2 +x_{22}V_2^2+x_{33}V_3^2+x_{ll}l^2+x_{12}V_1V_2+x_{13}V_1V_3 +x_{23}V_2V_3\}_i.$$

It is obvious that for arbitrarily chosen perturbing potentials λH_1 and λ^2H_2, the cross product terms will in general not vanish; and the above equations will not be valid. The perturbing potentials for a molecule of the carbon dioxide type have, however, been assumed to possess certain special properties; namely, they are analytic functions endowed with the geometric symmetry of the molecule, λH_1 contains no power greater than the third, and λ^2H_2 contains no power higher than the fourth. A detailed study shows that these properties of the potential function cause each of the cross product terms to vanish. The actual proof of this statement will be omitted since the analysis, while quite straightforward, is rather lengthy.

The connection between theory and experiment, and the determination of the anharmonic constants can be facilitated by the consolidation of the energies of the zeroth and second orders. This may be accomplished by means of the relation $\sum_i C_{\tau t_i}^2=1$. For, from this it follows at once that $W_0^n=\sum_i C_{\tau t_i}^2 W_0^n$, and hence that

$$W_0^n+\lambda^2W_2^{n\tau}=h\sum_i C_{\tau t_i}^2\{x'+\nu_1V_1+\nu_2V_2+\nu_3V_3 +x_{11}V_1^2+x_{22}V_2^2+x_{33}V_3^2+x_{ll}l^2+x_{12}V_1V_2 +x_{13}V_1V_3+x_{23}V_2V_3\}_i$$

where

$$x'=x_0+2\omega_2+\omega_3/2,$$

$$\nu_1=x_1+2\omega_2,\quad \nu_2=x_2+\omega_2,\quad \nu_3=x_3+\omega_3.$$

ω_2 and ω_3 are the zeroth order simple harmonic frequencies which are the solution to the problem of small vibrations.

Omitting the cumbersome details of obtaining the matrix elements[6] and summing them, the functional dependence of the coefficients may be given as follows. (As listed here the relationships are appropriate for the nonresonant type of triatomic, linearly symmetric molecules, such as CS_2, and their adaption to CO_2 is achieved by first discarding all terms containing the denominator $\omega_1-2\omega_2$, and then replacing ω_1 by $2\omega_2$.)

$$x'=\omega_1/2+\omega_2+\omega_3/2+3d/4+3f/4+2e+g/2+i/2+h/4+(11a^2/8+b^2/2+c^2/2+3ab/2 +3ac/4+bc/2)/\omega_1+b^2/2(\omega_1+2\omega_2)+c^2/4(\omega_1+2\omega_3)+h\omega_3/16\pi^2I\omega_2,$$

$$\nu_1=\omega_1+3d/2+g+h/2-3a(9a/8+b+c)/\omega_1-3a^2/8\omega_1-b^2/2(\omega_1+2\omega_2)+b^2/2(\omega_1-2\omega_2) -3c^2/8(\omega_1+2\omega_3)+c^2/4(\omega_1-2\omega_3),$$

$$\nu_2=\omega_2+3e+g/e+i/2-b(b+3a/2)/\omega_1-b^2/4(\omega_1+2\omega_2)+h\omega_3/16\pi^2I\omega_2,$$

$$\nu_3=\omega_3+3f/2+h/2+i-c(c+6a+4b)/4\omega_1-3c^2/8(\omega_1+2\omega_3)+c^2/8(\omega_1-2\omega_3)+h\omega_3/8\pi^2I\omega_2,$$

$$x_{11}=3(d-19a^2/4\omega_1)/2,$$

[6] In computing the second order energy constant it is necessary to obtain the matrix elements of the various powers of the coordinates σ, ξ and ρ. These may be readily found by referring to the known properties of the Hermitian and Laguerre orthogonal functions. See for example E. Schrödinger, Ann. d. Physik [4] **80**, 437 (1926). Math. appendix, and E. Fues, Ann. d. Physik **80**, 367 (1926).

$$x_{22}=3e/2-b^2/2\omega_1-b^2/8(\omega_1+2\omega_2)-b^2/8(\omega_1-2\omega_2),$$

$$x_{33}=3f/2-c^2/2\omega_1-c^2/8(\omega_1+2\omega_3)-c^2/8(\omega_1-2\omega_3),$$

$$x_{ll}=-e/2+b^2/8(\omega_1+2\omega_2)+b^2/8(\omega_1-2\omega_2),$$

$$x_{12}=g-3ab/\omega_1-b^2/4(\omega_1+2\omega_2)+b^2/4(\omega_1-2\omega_2),$$

$$x_{13}=h-3ac/\omega_1-3c^2/8(\omega_1+2\omega_3)+c^2/2(\omega_1-2\omega_3),$$

$$x_{23}=i+h\omega_3/8\pi^2I\omega_2.$$

These equations constitute relations between the constants which fix the energy levels (and which we may hope to obtain from observational data), and the anharmonic constants of the molecule. The question now arises as to whether these equations imply any connections between the x's and ν's themselves. We have noticed only one such interdependence, but this will prove to be of considerable value. x_{22} and x_{ll} are related through the first order perturbation constant b and the normal frequency ω_2 by the expression $x_{22}+3x_{ll}=-3b^2/16\omega_2$ (this is the form in which it applies to the carbon dioxide molecule). $-3b^2/16\omega_2$ can be reduced to a number directly inasmuch as ω_2 is known to be about 667.5 cm^{-1} while the quite precise value of $|b|=72.5$ cm^{-1} is given by Dennison.[2] Thus for the CO_2 molecule $x_{22}+3x_{ll}=-1.47$ cm^{-1}. The observational data which help to determine the numerical values of the x's and ν's are the experimental locations of the infrared vibration-rotation band centers; for, each such position is given theoretically by the difference between two energies of the type:

$$W_1^{n\tau}+\sum_i C_{\tau l_i}^2\{x'+\nu_1V_1+\nu_2V_2+\nu_3V_3+x_{11}V_1^2+x_{22}V_2^2+x_{33}V_3^2+x_{ll}l^2+x_{12}V_1V_2+x_{13}V_1V_3+x_{23}V_2V_3\}_i.$$

(Because of the perturbations, the energy of the ground state is raised by the amount $\Delta/2+x'$.) About half of the extensively known band system of CO_2 is to be employed in this evaluation of the coefficients, and the latter will then be used to predict the remaining known bands as well as bands yet undiscovered. None of the difference bands will be used in the solution, since they yield no independent relations, but only combinations of those obtainable from the fundamentals and their overtones. Hence, the equations to be used in solving for the coefficients will be simply those which give the separations of the energy levels from the ground state, and they have the form:

$$(W_1^{n\tau}-\Delta/2)+\sum_i C_{\tau l_i}^2\{\nu_1V_1+\nu_2V_2+\nu_3V_3+x_{11}V_1^2+x_{22}V_2^2+x_{33}V_3^2+x_{ll}l^2+x_{12}V_1V_2+x_{13}V_1V_3+x_{23}V_2V_3\}_i=$$

observed position of level, where $W_1^{n\tau}$ depends upon Δ, l and $|b|$.

We proceed to discuss the adaptation of these equations to the problem of the carbon dioxide molecule.

Correlation

The data on the infrared spectrum of CO_2 come from several sources. Barker,[7] and Martin and Barker[8] have explored the region between 2.7μ and 15μ, mapping a number of bands which range from the $\nu_3+(\nu_1, 2\nu_2)$ combination bands to the ν_2 fundamental. Recently, Wu and Barker[9] have discovered the overtone $3\nu_3$, and have succeeded in getting accurate measurements on the bands $\nu_3+(4\nu_2, 2\nu_2+\nu_1, 2\nu_1)$ at 2μ and the bands $\nu_3+(6\nu_2, 4\nu_2+\nu_1, 2\nu_2+2\nu_1, 3\nu_1)$ at 1.6μ. These new data on the 2μ group of bands displace the older work of Schaefer and Philipps[10] whose measurements appear to be in error by approximately one hundred waves per centimeter. This accounts for the very large discrepancy between the calculated positions of these bands (correct to first order) and the values of Schaefer and Philipps as noted by Dennison.[2]

Making a tentative solution for the x's and ν's on the basis of these observations by Barker, Martin and Wu, it has been demonstrated that the three doublet bands photographed by Adams and Dunham[11] in the atmosphere of the planet Venus are indeed to be attributed to the CO_2 molecule and are to be identified as $5\nu_3$ and $5\nu_3+(\nu_1, 2\nu_2)$. Detailed information concerning all of the known bands of carbon dioxide is collected in Table I together with the names of the observers.

In determining the constants, the x's and ν's, it would be possible to equate all the observed

[7] E. F. Barker, Astrophys. J. **55**, 391 (1922).

[8] P. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932).

[9] To be published in the near future.

[10] Cl. Schaefer and B. Philipps. Zeits. f. Physik **36**, 641 (1926).

[11] W. S. Adams and T. Dunham, Jr., Pub. A.S.P. **44**, 243 (1932).

positions of the levels to their theoretical values and solve the resulting equations by the method of least squares. This method appears to be impractical, however, for two reasons, first because of the great numerical labor involved and second because, as we shall see, the positions of the levels alone are not suitable for determining certain of the constants with any degree of accuracy. Instead the following method was employed.

Two very significant consequences of Dennison's[2] first order solution are immediately applicable. The first of these is the very accurate value of $|b|$; and the second is the estimate of Δ. Though Δ may be uncertain in this order of approximation, it is nevertheless of a lesser order of magnitude than $|b|$, and hence than W_1^{nr}. It is thus feasible to expand W_1^{nr} in powers of $\Delta/|b|$, retaining no terms beyond the first power. Direct use is made of this knowledge in simplifying the equations discussed below and in obtaining a preliminary value of Δ for the present solution.

Eleven of the most accurately known and most suitably placed bands are selected in setting up the observational equations, and these together with the relation $x_{22}+3x_{ll}=-1.47$ cm^{-1} give twelve equations in the twelve unknowns: $\nu_1\nu_2\nu_3$; $x_{11}x_{22}x_{33}x_{ll}$; $x_{12}x_{13}x_{23}$; $\Delta|b|$. Careful examination shows that this group of equations are algebraically inconsistent with any set of real values for the constants. The difficulty can easily be traced to the quantity Δ which is nearly indeterminate from the energy levels alone. This is because very small changes in the energy levels (of the order of magnitude of the experimental error) cause large fluctuations in Δ, even allowing it to become imaginary. It was thus necessary to find an alternative method for the definition of the numerical value of Δ, or at least of its order of magnitude. This method is furnished by the ratio of intensities of the strong Raman doublet in CO_2 in the neighborhood of 1300 cm^{-1}. The experimental value of this ratio has been given by Dickinson, Dillon and Rasetti[12] as 2/3. The amplitudes entering into the intensity expressions for the Raman lines are proportional to the constants C_{rt}; that is, to the amount in which the wave function active for the Raman effect enters into the wave function of the level in question. The ratio of the intensities is therefore equal to the ratio of the squares of C_{rt} and may be shown in this case to have the form $(1-\Delta/2^{\frac{1}{2}}|b|)/(1+\Delta/2^{\frac{1}{2}}|b|)$. In this way it is found that $\Delta\cong 17$ cm^{-1}. With this order of magnitude of Δ serving as a criterion, very small (about $\frac{1}{2}$ cm^{-1}) but arbitrary corrections were made in the observed positions of some of the eleven energy levels mentioned above. These corrections were maintained as small as possible while keeping Δ near 17 cm^{-1} and $|b|$ close to 72.5 cm^{-1}. The modified and now consistent equations are given below, where we have introduced the notation $\beta=|b|$ and $y=\Delta/\beta$.

(1) $\nu_2+x_{22}+x_{ll}=667.9$ cm^{-1},

(2) $\Delta/2-\beta(1+y^2/4)/2^{\frac{1}{2}}+(1-y/2^{\frac{1}{2}})(\nu_1+x_{11})/2+(1+y/2^{\frac{1}{2}})(2\nu_2+4x_{22})/2=1268.3$,

(3) $\Delta/2+\beta(1+y^2/4)/2^{\frac{1}{2}}+(1+y/2^{\frac{1}{2}})(\nu_1+x_{11})/2+(1-y/2^{\frac{1}{2}})(2\nu_2+4x_{22})/2=1387.9$,

(4) $2\nu_2+4x_{22}+4x_{ll}=1335.8$,

(5) $\nu_3+x_{33}=2350.1$,

(6) $\Delta/2-\beta(1+y^2/8)+(1-y/2)(\nu_1+x_{11}+\nu_2+x_{22}+x_{12}+x_{ll})/2+(1+y/2)(3\nu_2+9x_{22}+x_{ll})/2=1933.2$,

(7) $\Delta/2+\beta(1+y^2/8)+(1+y/2)(\nu_1+x_{11}+\nu_2+x_{22}+x_{12}+x_{ll})/2+(1-y/2)(3\nu_2+9x_{22}+x_{ll})/2=2077.4$,

(8) $5\nu_3+25x_{33}=11496.5$,

(9) $\Delta/2-\beta(1+y^2/4)/2^{\frac{1}{2}}+(1-y/2^{\frac{1}{2}})(\nu_1+x_{11}+5\nu_3+25x_{33}+5x_{13})/2$
$+(1+y/2^{\frac{1}{2}})(2\nu_2+4x_{22}+5\nu_3+25x_{33}+10x_{23})/2=12672.4$,

[12] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

$$(10)\quad \Delta/2+\beta(1+y^2/4)/2^{\frac{1}{2}}+(1+y/2^{\frac{1}{2}})(\nu_1+x_{11}+5\nu_3+25x_{33}+5x_{13})/2 + (1-y/2^{\frac{1}{2}})(2\nu_2+4x_{22}+5\nu_3+25x_{33}+10x_{23})/2=12774.7,$$

$$(11)\quad 4\Delta/3+(4\nu_2+16x_{22}+\nu_3+x_{33}+4x_{23})/3+2(2\nu_1+\nu_3+4x_{11}+x_{33}+2x_{13})/3=4982,$$

$$(12)\quad x_{22}+3x_{11}=-1.47.$$

These equations yield the following values for the molecular constants.

$\beta=72.9\ \text{cm}^{-1}$	$\nu_3=2362.8$	$x_{11}=-0.74$
$\Delta=14.7$	$x_{11}=-1$	$x_{12}=-2.3$
$\nu_1=1321.7$	$x_{22}=+0.74$	$x_{13}=-22.1$
$\nu_2=667.9$	$x_{33}=-12.7$	$x_{23}=-10.9$

While the twelve equations which have been used are consistent and hence yield unique values for the constants, a closer examination discloses the fact that these constants are not determined with equal accuracy. Small changes in the observed positions of the bands (of the order of the experimental error) would sensibly alter some of them, while leaving others virtually unchanged. ν_1 and ν_2 might be out by as much as one wave per centimeter, but ν_3 is probably accurate to about two-tenths of one wave per centimeter. The anharmonic constants β, x_{33}, $x_{13}+2x_{23}$, and $x_{22}+3x_{11}$ are known to within a few tenths of one wave per centimeter. The remaining constants are less precisely determined, in some cases only to order of magnitude.

The positions of any of the vibrational levels of the carbon dioxide molecule may now be computed with the aid of the constants just determined. In Table I we have collected the observational data on the positions of the levels in order to compare them with our calculated results. The identification of the levels is given in column I, while the heights of the energy levels above the ground state, observed and calculated, respectively, are contained in columns II and III. The sources of the experimental data are listed in the last column.

In comparing the calculated and observed locations of the vibrational levels, the latter should be divided into two classes. The first of these contains those bands which are employed in the evaluation of the constants; the discrepancies in this group are all of the order of the experimental error, and represent the small arbitrary additions used to make the simultaneous equations consistent. The agreement between the calculated and observed values for the remaining nine levels is extraordinarily good, being better than the experimental error in eight instances and poorer in only one (the difference of eight waves per centimeter in the case of the 4860 band of the 2μ group of bands is the only example of inferior agreement). This good agreement which obtains in the second class of levels is genuine and not fortuitous. It is to be considered a substantiation of the method of attack used in the problem, and a verification of the expression

TABLE I. *Observed and calculated values for the energy levels in CO_2.*

Identification $V_1\ V_2\ V_3\ l$	Position (cm^{-1}) Calculated	Observed	Observer (number indicates reference)
0 1 0 1	667.9	667.5	8
0 2 0 0	1286.3	1285.8	8
1 0 0 0	1387.9	1388.4	
0 2 0 2	1335.8	1336.2	8
0 3 0 1	1933.2	1933.5	8
1 1 0 1	2077.4	2077.1	
0 0 1 0	2350.1	2350.1	8
0 2 1 0	3614	3610	7
1 0 1 0	3716	3717	
0 4 1 0	4852	4860	9
1 2 1 0	4982	4982	
2 0 1 0	5109	5110	
0 6 1 0	6078	6079	9
1 4 1 0	6233	6233	
2 2 1 0	6352	6353	
3 0 1 0	6512	6512	
0 0 3 0	6974	6978	9
0 0 5 0	11496.5	11496.5	11
0 2 5 0	12672.4	12672.4	11
1 0 5 0	12774.7	12774.7	

TABLE II. *Positions of some bands which ought to be accessible to experiment.*

Identification V_1	V_2	V_3	l	Calculated position (cm^{-1})
0	2	3	0	8188
1	0	3	0	8291
0	3	4	1	11050
1	1	4	1	11193
0	4	5	0	13823
1	2	5	0	13952
2	0	5	0	14080
0	1	6	1	14322
0	6	5	0	14961
1	4	5	0	15115
2	2	5	0	15234
3	0	5	0	15397
0	0	7	0	15917
0	2	7	0	17049
1	0	7	0	17151
0	0	9	0	20236
0	2	9	0	21324
1	0	9	0	21426

for the energy of the carbon dioxide molecule.[13]

In Table II are given the positions of some bands which ought to be accessible to experiment, but which have as yet not been discovered. The bands in the visible and photographic infrared regions of the spectrum will have to be sought in the absorption spectrum of the planet Venus, and such a search is being made by T. Dunham, Jr., at Mount Wilson Observatory. On the other hand, the bands $3\nu_3+(\nu_1, 2\nu_2)$ should offer no particular difficulty, and should be as easily observed as the bands at 1.6μ.

CONCLUSION

The second order energy constant for the carbon dioxide molecule has been computed. It involves eleven constants whose connections with the twelve constants defined by the potential energy is given. It is consequently not possible to obtain the potential energy function from our present results, and recourse must be had to some alternative method. This method consists in an analysis of the interaction between vibration and rotation. It may be shown that the convergence in the fine structure lines of the various absorption bands will yield values for the three constants of the first order potential function; namely, a, b and c. A determination of the entire potential function is thus made possible. This investigation will be the subject of a second paper, to appear, shortly in which, also, an attempt will be made to describe the potential energy of the carbon dioxide molecule by means of a function resembling the Morse potential function for diatomic molecules.

Finally, the writers wish to express their indebtedness and thanks to Professor E. F. Barker and Mr. Ta-You Wu for placing the results of their investigation at our disposal and allowing us to publish a preliminary account of them, and to Dr. T. Dunham, Jr. for his willing and helpful correspondence in connection with the Venus bands.

[13] In a recent paper Langseth and Nielsen (Zeits. f. physik. Chemie **B19**, 427 (1932)), have reexamined the Raman spectrum of gaseous carbon dioxide, using an exposure time of one month. In addition to the four Raman lines previously known, they obtained six very faint lines which should, presumably, be due to transitions starting from the three excited levels in the neighborhood of 1300 cm^{-1}. The observed positions of the six extremely faint lines are: 1241, 1305, 1325, 1344, 1369 and 1433 cm^{-1}. On the other hand, the frequencies of the above-mentioned transitions may be readily computed from our formulae, and eight very faint Raman lines should appear in the following positions: 1166, 1248, 1268, 1288, 1390, 1415, 1426 and 1517 cm^{-1}. It thus appears that of the eight lines which should appear, the lines 1268, 1288, 1390 and 1415 blend with the four already known Raman lines; the lines 1166 and 1517 do not fall within the limits of the region covered by the experimental data, while the lines 1248 and 1426 probably correspond to the two observed lines 1241 and 1433. The lines 1241 and 1433 are classified as *ausserordentlich schwach* and hence the discrepancy between the observed and computed values is not to be considered as a serious disagreement. There appears to be no place in the theoretical scheme for the remaining four observed lines, inasmuch as we have been able to find no transitions corresponding to these frequencies. It is perhaps possible that this discrepancy originates in the intrinsic difficulty experienced in recording faint lines through exposures of such extended duration.

Diffraction of Electrons by Metal Surfaces

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Fast electrons scattered from polished metal surfaces do not form diffraction patterns. A strong Debye-Scherrer pattern is produced, however, by electrons scattered from a surface which has been mechanically roughened in such a manner that electrons are able to pass directly through projecting irregularities. Small ridges extending from wires, which have been drawn through an imperfect die, also give rise to a diffraction pattern. These experiments indicate: (1) that there is no considerable layer of amorphous material (Beilby layer) on a polished metal surface, and (2) that Debye-Scherrer diffraction patterns are formed only by transmitted electrons. Fast electrons scattered at a small glancing angle from an *etched* polycrystalline surface form a diffraction pattern if the surface appears mat or roughened, but no pattern is formed if the surface shows metallic luster. Here again diffraction patterns appear to be produced only by transmission. A probable explanation is given for the fact that diffraction rings are not formed by electrons scattered from smooth polycrystalline surfaces.

IT is a well-established fact that electrons scattered by polished metal surfaces do not form diffraction patterns—the scattering is diffuse and featureless as far as the eye can detect. This result can be explained on the hypothesis that the atoms in the surface of the metal, which act as scatterers, have been completely disorganized by the polishing until they form a layer of amorphous metal as supposed by Beilby. This explanation of the phenomenon has been proposed by G. P. Thomson[1] and by R. C. French.[2] It is my purpose in this paper; (1) to present certain experimental evidence opposed to this interpretation, (2) to point out a correlation between the failure of polished surfaces to form diffraction patterns and a similar failure in the case of certain heavily etched surfaces, and (3) to present a new explanation for the absence of diffraction patterns from polished surfaces.

A beam of fast electrons (wave-length 0.05A) is directed upon the polished surface of a metal block at glancing angle about one and a half degrees. The scattered electrons are received upon a photographic plate, and no detectable diffraction pattern is produced. Parallel scratches are then made on the surface by rubbing the block upon rather coarse emery paper. Electrons scattered from the block in this condition form a Debye-Scherrer diffraction pattern characteristic of the metal. A strong sharp pattern is formed when the scratches lie normal to the plane of incidence, a very much weaker one (relative to the background scattering) when they lie parallel to this plane.

The pattern obtained from a scratched nickel surface with the scratches normal to the plane of incidence is reproduced in Fig. 1. A similar pattern for tungsten is shown in Fig. 2. In the former there is one weak ring of unknown origin and there are eighteen rings due to the face-centered cubic structure of nickel. In the latter are fifteen rings all of which arise from the body-centered tungsten lattice. In each figure the position of the primary beam has been registered by switching on the current for an instant after

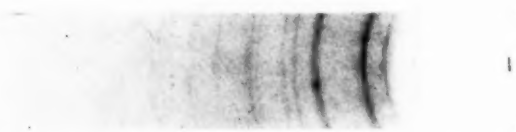

FIG. 1. Diffraction pattern formed by electrons scattered from a scratched nickel block, the scratches of which are normal to the plane of incidence.

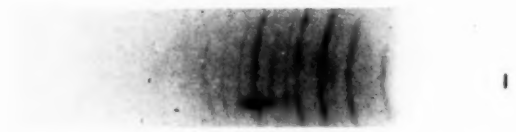

FIG. 2. Similar diffraction pattern from a scratched tungsten block.

[1] G. P. Thomson, Proc. Roy. Soc. **A128**, 658 (1930).
[2] R. C. French, Nature **129**, 169 (1932).

removing the specimen block. The photographs obtained with the scratches parallel to the plane of incidence are not reproduced. These show a diffusely scattered background of full speed electrons upon which a few very weak rings of the characteristic patterns can just be detected.

The interpretation seems obvious: The surface material has been thrown up into ridges by the scratching operation. Parts of these are thin enough to transmit the electrons incident upon them, and to give rise to a pattern after the manner of thin films. As the ridges lie almost entirely parallel to the direction of scratching the pattern is intense when this direction is normal to the plane of incidence, and extremely weak when it is parallel to the plane of incidence. In other words, the diffraction patterns are produced by electrons which have passed entirely through projecting ridges of metal, and when the ridges are so turned that electrons cannot go directly through them no pattern is formed. Furthermore the ridges are made up of material which lay in or very near the polished surface. This material gives rise to the usual ring pattern, and some of it, therefore, is crystalline. We cannot say perhaps that it is all crystalline, but we can say that it is certainly not all amorphous.

Another recent experiment also offers evidence against the amorphous layer theory. In this experiment electrons were scattered from the surfaces of drawn wires of nickel and of copper. The beam of electrons (0.05A) was normal to the wire and just grazed its surface. A wire which, immediately before testing, had been drawn through a good die gave a general scattering of full speed electrons, but there was no trace of diffraction rings. Other wires were tested which had been drawn through a broken die and had projecting from their surfaces minute fins, caused by the forcing of metal into the cracks of the die. These under favorable conditions gave complete Debye-Scherrer circles, *part of each circle lying in the geometrical shadow of the wire.* A pattern of this sort could be produced only by transmission of electrons through these fins.

The material of the fins had been cold worked to an extreme degree, comparable perhaps with the working of a surface during polishing. Yet, from the existence of the diffraction pattern, we know that at least the greater part of the material of the fins was ordinary crystalline metal.

These two experiments indicate strongly that a polished metal surface is not covered by any appreciable layer of amorphous material.

But polished surfaces are not alone in failing to produce detectable patterns; even heavily etched surfaces give rise, in some cases, to diffuse scattering only. The scattered electrons which darken the photographic plate have, in these cases, the same speed as the electrons in the primary beam. (This fact I have established by comparing the deflections received by the primary and by the scattered electrons in transverse electric fields.) Yet no detectable pattern is produced. There can be no question here of an amorphous layer.

Whether or not a given etched surface will produce a pattern can be predicted with considerable certainty from its appearance. If the etched surface is mat or frosted, it will almost certainly produce a pattern; if it is smooth and shows metallic luster, almost certainly not. (These smooth surfaces are sometimes produced when the etching is very rapid.) The frosted surfaces must present to the incident beam many sharp crystal edges, while the smooth surfaces do not. One is led to conclude that diffraction patterns are produced only by electrons which have passed entirely through crystal edges projecting from the surface. Certainly those surfaces which do not have such projections are incapable of giving diffraction rings. *A similar conclusion was reached independently in the experiments on scratched surfaces.* The idea that surfaces covered by minute projections would be favorably formed for the production of diffraction rings was first put forward by G. P. Thomson.[1]

The conclusion that diffraction patterns of the Debye-Scherrer type are in fact always transmission patterns is particulary acceptable because it affords an explanation of the fact that such patterns never reveal evidence of refraction. It is easy to show that a potential difference of ten or fifteen volts between the outside and inside of the metal should have a marked effect upon the pattern *provided* the electrons which form the pattern have passed in and out of the metal through the same surface; yet such an effect has

not been observed. If, as the present experiments pretty well prove, the patterns are produced in all cases by transmission then effects due to refraction should be too small to be observed.

But, if we accept this conclusion that all Debye-Scherrer patterns are formed by transmitted electrons, we are at once faced by the problem of accounting for the absence of such patterns when electrons enter and leave a metal through the same surface. The failure of these electrons to form patterns may very likely be the result of refraction and of minute surface irregularities. For electrons entering and leaving a metal through the same surface, the calculated effect of a potential difference between the outside and inside of the metal is a considerable displacement (and change of shape) of all diffraction rings. The amount of the displacement turns out to be a function of the glancing angle upon the surface. If the glancing angle varies slightly from one section of the surface to another, because of surface irregularities, the result is a broadening of all the displaced diffraction rings. It seems quite possible that broadening produced in this way might be sufficient to cause each ring to overlap the neighboring rings, so that only general darkening of the photographic plate could be detected.

I have worked out this idea for the special case of 50 kilovolt electrons (0.055A) incident upon nickel, assuming a potential difference of 15 volts at the surface of the metal. It comes out that, if parts of the surface were inclined to the mean plane of the surface by a maximum amount of as much as one-half of a degree, the average width of diffraction rings would be of the order of 2 mm and most rings would overlap neighboring rings. If considerable portions of the surface were inclined to its mean plane by as much as half a degree this broadening would be sufficient to make the observation of diffraction rings doubtful.

I have tested a very highly polished steel surface in the hope of finding diffraction rings showing the influence of refraction. No rings have appeared. The test has, however, yielded evidence that at least some well polished metal surfaces possess sub-microscopic irregularities involving variations of glancing angle of several degrees. The observation is a very simple one —near the forward direction the intensity of scattering varies greatly with the degree of polish. An unusually fine surface scatters much more efficiently than does one which is less perfect. I believe that this difference must be attributed to shadows cast by irregularities on the less perfect surface. This shadowing extends at least as far as several degrees above the surface, which means that there is a corresponding variation of glancing angle. Such a variation is sufficient to account for the absence of a diffraction pattern from the less perfect surface. And it seems altogether possible that the better surface would also be found to be very imperfect if we could obtain a still better standard against which to compare it.

Theory of the Energy Distribution of Photoelectrons*

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(Received February 21, 1933)

Because of the thermal energies of the electrons in a metal there can be no *sharply defined* maximum emission energy of photoelectrons, as was once supposed. On the basis of the Sommerfeld theory and the Fermi-Dirac statistics, expressions are derived for the form of the energy distribution and current voltage curves in the vicinity of the apparent maximum energy. The method used is similar to that used by Fowler in computing the total emission current. In Part I the energies normal to the emitting surface are considered. At 0°K the theoretical current-voltage curve is a parabola tangent to the energy axis at V_{max}, while for higher temperatures it approaches the axis asymptotically. In Part II the treatment is extended to the total energy of emission and in this case the current-voltage curve at 0°K is a parabola concave toward the voltage axis and cutting it at a large angle. At higher temperatures there is an asymptotic approach. Even at room temperature there is an uncertainty of several hundredths of a volt in V_{max}, though the theory yields a method of determining the maximum energy which would be observed at 0°K. Both parts of the theory are found to be in agreement with new experiments on molybdenum. The bearing of the theory on the photoelectric determination of h is discussed.

INTRODUCTION

THE problem of the energy distribution of photoelectrons became of great interest to physicists with the propounding of the Einstein equation in 1905. The work of Richardson and Compton,[1] Hughes,[2] Millikan[3] and others has shown clearly that photoelectrons emerge from metal surfaces with all velocities from zero up to a more or less sharply defined maximum velocity, whose value varies with the frequency of the incident light according to the Einstein equation. Since this equation involves only the *maximum* velocity of emission, the attention of physicists working in this field has been largely confined to the problem of measuring this maximum energy with great precision for incident light of different frequencies. Their success in this direction has been so great that the photoelectric method is now regarded as one of the most accurate available for the determination of the value of the universal constant, h/e.

However, it must now be quite generally recognized that there can really be no such thing as a *perfectly sharply defined* maximum emission energy for photoelectrons, except at 0°K, because of the thermal energies of the electrons in the metal. While it might appear at first sight that, at room temperature, the thermal energies would introduce a relatively small uncertainty in the determination of the maximum emission energy, nevertheless even a superficial calculation shows that the uncertainty may be of the order of a few hundredths of a volt. Since the more accurate determinations of h/e have involved measuring the maximum energy to less than 0.01 volt, it becomes of great importance to inquire more in detail as to how much significance can be attached to a "maximum" energy determined with this precision.

In order to answer this problem satisfactorily it is of course necessary to obtain a theoretical expression for the energy distribution function of the photoelectrons and to examine the behavior of this function as it approaches the energy axis. While it is known from experiment that the general form of the distribution curve is that shown in Fig. 1, yet all attempts to deduce a theoretical expression for the curve have met with indifferent success. On the basis of the classical electron theory of metals it was assumed that the kinetic energy of thermal agitation of

* Presented in part at the Chicago meeting of the American Physical Society, November 25, 1932. See Phys. Rev. **42**, 905 (1932).

[1] O. W. Richardson and K. T. Compton, Phil. Mag. **24**, 575 (1912).

[2] A. L. Hughes, Phil. Trans. Roy. Soc. **212**, 205 (1912).

[3] R. A. Millikan, Phys. Rev. **7**, 362 (1916).

the electrons in the metal was negligible in comparison to the energy $h\nu$ received from the incident light, hence it would be expected that *all* electrons would emerge with the *same* velocity, —that given by the Einstein equation,

$$\tfrac{1}{2}mv^2 = h\nu - \phi e,$$

where ϕ is the work function of the surface. The fact, however, that most of the electrons emerged

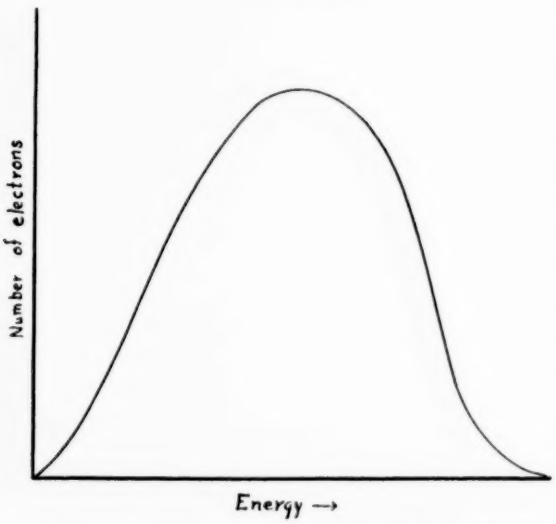

FIG. 1. General form of observed energy distribution curve for photoelectrons.

with a velocity less than this was readily understood on the assumption that the electrons lost energy by collisions within the metal before they reached the surface. However, since the nature of these collisions is unknown, no quantitative expression for the energy distribution can be obtained without introducing special assumptions which cannot be directly tested.

With the advent of the Sommerfeld electron theory it appeared that, because of the long mean free path of the electrons, collision phenomena should play a negligible rôle, and that the energy distribution of the emergent electrons should be directly deducible in terms of the distribution within the metal as given by the Fermi statistics. Fowler[4] has discussed this question qualitatively, but it now appears desirable to attempt a more quantitative treatment.

It should be stated at the outset that at present it is not feasible to attempt to derive a quantitative expression for the complete energy distribution curve, for, granted that collision phenomena may be neglected, it would still be necessary to know (1) the way in which the probability that an electron absorb an incident quantum depends on the initial velocity of the electron itself, and (2) the way in which the transmission coefficient of the electron through the surface potential step W_a depends on the electron velocity. In principle, both factors can be computed from wave mechanics, but the first depends on the detailed structure of the force field within the metal and the second on the exact form of the surface potential step and, for any particular metal, very little is known about either of these. However, as pointed out above, we are not at present interested in the whole form of the distribution curve, but only in its behavior in the vicinity of the "maximum" energy. If we confine our attention to this portion of the curve, it turns out that both above factors vary relatively slowly, and hence can be considered constant. This is particularly true if we also consider only the effect of frequencies near the threshold. Fowler[5] has already made use of these assumptions to derive an expression for the spectral distribution curves in the vicinity of the threshold, obtaining an expression which is in excellent agreement with experiment.[5, 6] It was the remarkable success of Fowler's theory which led the present author to attempt to extend Fowler's methods to the problem of energy distribution.

It will be convenient to divide the treatment of the problem into two parts. In Part I we consider only the energies normal to the emitting surface, since these can be treated simply theoretically and can be readily analyzed experimentally. In Part II the treatment is extended to the total energy of the emitted electrons.

[4] R. H. Fowler, Proc. Roy. Soc. **118**, 229 (1928). A more complete theory for energy distribution from *thin films* has been given by Fröhlich, Ann. d. Physik **7**, 103 (1930).

[5] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[6] L. A. DuBridge and W. W. Roehr, Phys. Rev. **39**, 99 (1932); **42**, 52 (1932); A. H. Warner, Phys. Rev. **38**, 1871 (1931).

I. Distribution of Normal Energies

1. Statement of the problem

Let a plane metal plate A (Fig. 2) be placed in an evacuated bulb and illuminated by light of frequency ν which is greater than the threshold frequency ν_0 (defined below). Let the emitted photoelectrons be collected by a second plate B, parallel to the first, a variable potential being applied between the plates. If B is positive with respect to A, all the emitted electrons are collected and the current is independent of the potential (saturation current). If B has a potential V, negative to A, only those electrons reach B which emerge from A with velocity component v_n, normal to the surface, such that $\frac{1}{2}mv_n^2 = E_n \geqq Ve$. E_n is called for brevity the "normal energy." (In all that follows it will be assumed that the contact potential between the two surfaces has been included in V, so that V is the *actual*, not the *applied*, retarding potential.) Let $F(V)$ be the number of electrons reaching B when the retarding potential is V. If $F(V)$ is measured as a function of V a "current-voltage curve" of the form shown by curve I in Fig. 3 is generally obtained.[7]

Now let V' be the potential required just to stop an electron whose energy is E_n, so that V' is simply E_n expressed in equivalent electron-volts. Let $f(V')dV'$ be the number of electrons emerging with a normal energy V' in the range

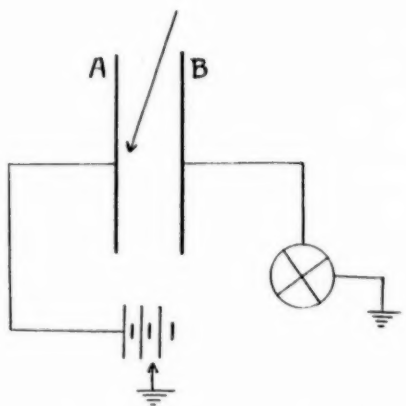

Fig. 2. Parallel plate method.

[7] For a summary of the experimental data see Hughes and DuBridge, *Photoelectric Phenomena*, pp. 11–22 and 114–135.

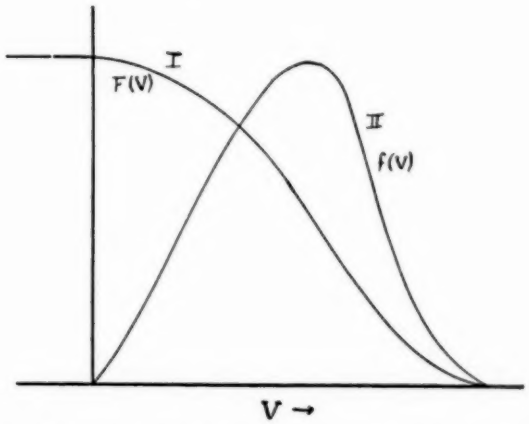

Fig. 3. General form of observed current-voltage curve (I) and the derived energy distribution curve (II).

dV'. Then $f(V')$ is the distribution function for normal energies. Obviously,

$$F(V) = \int_V^\infty f(V')dV' \tag{1}$$

and hence,

$$f(V') = -[dF(V)/dV], \tag{2}$$

the derivative being taken at the point where $V = V'$. Or we may write simply

$$f(V) = -dF(V)/dV.$$

Plotting $f(V)$ against V will then give a curve of the form shown by curve II of Fig. 3.[8]

We will assume:

(1) That the number of electrons per unit volume within the metal having a total kinetic energy ϵ in the range $d\epsilon$ is given by the Fermi-Dirac function

$$n(\epsilon)d\epsilon = \frac{8\pi(2m^3)^{\frac{1}{2}}}{h^3} \frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^{-(\mu-\epsilon)/kT}+1}. \tag{3}$$

(2) That the illuminated surface is perfectly plane and characterized by a surface potential step W_a.

(3) That the chance of an electron absorbing a quantum $h\nu$ is independent of ϵ.

[8] In these curves and some of those that follow as well as in the theory, *retarding* potentials are for convenience taken as *positive*, contrary to usual practice. The derived distribution curves then give energy increasing to the right, as usual.

(4) That the ability of an electron to escape from the surface depends only on its kinetic energy ϵ_n' perpendicular to the surface, where

$$\epsilon_n' = \epsilon_n + h\nu.$$

(5) That the probability that an electron which comes up to the surface with the normal energy ϵ_n' shall actually escape is proportional to the transmission coefficient $D(\epsilon_n')$, and that $D=0$ for $\epsilon_n' < W_a$ and $D=1$ for $\epsilon_n' > W_a$.

2. Energy distribution at 0°K

On the basis of the Fermi statistics, Fowler and Nordheim[9] have shown that the number of electrons reaching unit area of a surface within the metal in unit time with a normal energy between ϵ_n and $\epsilon_n + d\epsilon_n$ is given by

$$n(\epsilon_n)d\epsilon_n = (4\pi mkT/h^3)\log_e[1+\exp(\mu-\epsilon_n)/kT]d\epsilon_n. \quad (4)$$

For $T=0$°K this reduces to

$$n_0(\epsilon_n)d\epsilon_n = (4\pi m/h^3)(\mu-\epsilon_n)d\epsilon_n. \quad (5)$$

$n(\epsilon_n)$ is plotted as a function of ϵ_n in Fig. 4. At absolute zero there are no electrons with an energy greater than μ, hence the least frequency of light, ν_0, which will give electrons energy sufficient to escape is given by

$$\mu + h\nu_0 = W_a \quad \text{or} \quad \nu_0 = (W_a-\mu)/h = \phi e/h. \quad (6)$$

This equation defines the *true* threshold frequency ν_0 and the *true* work function ϕ. As Fowler has shown,[5] for temperatures above absolute zero there is no sharply defined "threshold frequency," though he has developed a method by which ν_0 may be determined from measurements made at any temperature.

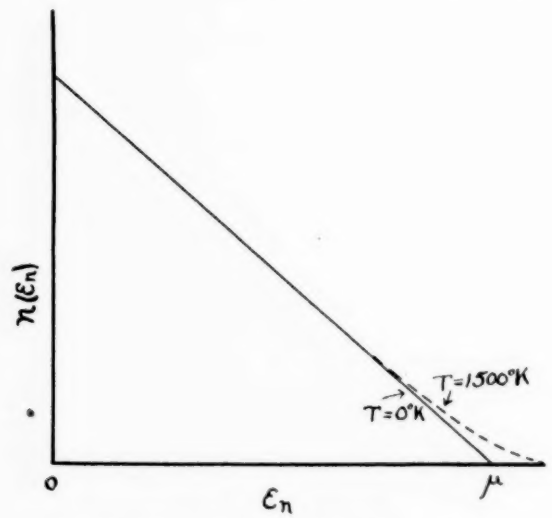

FIG. 4. Fermi-Dirac distribution of normal energies.

If the surface is illuminated by light of a frequency ν which is greater than ν_0, then an electron which originally had the normal energy ϵ_n will emerge with the energy E_n given by

$$E_n = \epsilon_n + h\nu - W_a. \quad (7)$$

We now assume that the number of electrons which emerge with the energy E_n in the range dE_n is proportional to the number coming up to the surface with the energy ϵ_n in the range $d\epsilon_n$. This involves simply assumptions (3), (4) and (5) mentioned above, together with the additional assumption that the energy $h\nu$ acquired from the light is also normal to the surface and so contributes directly to E_n. At first sight this last assumption might appear to be unjustified, since the energy acquired from the light might be in any direction. However, since we are confining our attention to the effect of frequencies not far from the threshold, the only electrons which escape will be those which do acquire energy from the light in a direction nearly normal to the surface, and particularly will this be true for the fastest of the emerging electrons. Hence for the cases we are considering the assumption introduces no appreciable error. If then $f_0'(E_n)dE_n$ is the number escaping with the normal energy E_n in the range dE_n we have at once from Eqs. (5) and (7),

$$f_0'(E_n)dE_n = \alpha(4\pi m/h^3)[\mu-(E_n-h\nu+W_a)]dE_n,$$

where α is a proportionality constant. Or setting $E_n = V'e$ and $W_a-\mu=\phi e$, we have

$$f_0(V')dV' = \alpha(4\pi me/h^3)[(h\nu-\phi e)-V'e]dV'. \quad (8)$$

This is the expression for the distribution of normal energies at the absolute zero, and yields

[9] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928); L. Nordheim, Phys. Zeits. **30**, 177 (1929). In plotting $n(\epsilon_n)$ Nordheim made an error which has been corrected in Fig. 4. The curve for $T=1500$°K can at no place fall *below* the 0°K curve, as is shown in his figure.

a distribution curve of the form shown in Fig. 5. It is evident that at this temperature there is a definite maximum energy of emission given by

$$eV_m' = E_{n_m} = h\nu - \phi e, \tag{9}$$

which is the Einstein equation.

Eq. (8) may at once be integrated to give the voltage current curve,

$$F_0(V) = \int_V^\infty f_0(V')dV' = \alpha(2\pi me^2/h^3)(V_m - V)^2, \tag{10}$$

which is the parabola shown by curve II of Fig. 5.

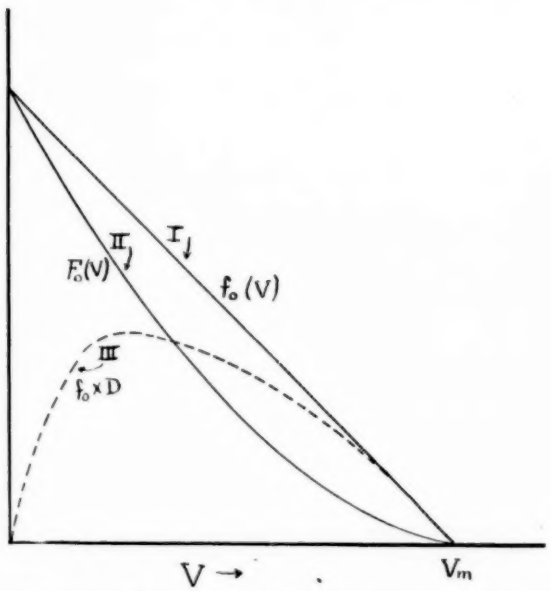

FIG. 5. I. Theoretical distribution of normal energies at 0°K. II. Current-voltage curve. III. Energy distribution corrected for transmission coefficient.

Evidently the curves predicted by this simple theory do not resemble at all, in their general form, the curves actually obtained from experiment. This is largely due to the fact that we have neglected any possible variation of the transmission coefficient D for electrons of different velocities. It is unfortunate that there is no direct method of determining D for any particular surface. However, if we use the values of D computed by Condon[10] and Nordheim[11] for a potential barrier of the form shown in Fig. 6, the energy distribution curve takes the form shown by curve III in Fig. 5, which more nearly resembles the experimental curves, though no quantitative comparison can be made. The point of interest at present, however, is the fact that for electrons emerging from the surface with energies exceeding a few tenths of a volt, D is very nearly unity, and hence does not affect the form of the distribution curve in the vicinity of V_m. This portion of the curve is, however, greatly affected by the temperature of the surface and this effect will now be examined more in detail.

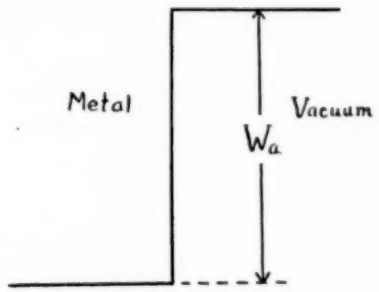

FIG. 6. Ideal surface potential step.

3. Effect of temperature

We have seen above that for a metal at 0°K there is a sharp upper limit to the energy of the emergent photoelectrons, and this varies with the frequency according to the Einstein equation. At higher temperatures, however, there is no longer a sharp upper limit to the energies of the electrons within the metal, and hence no sharp upper limit for the emergent energies, so that the photoelectric current-voltage current curves will have a "tail," and will approach the axis asymptotically. It is possible to deduce a quantitative expression for the form of this tail which can be compared directly with experiment. For this purpose we return to Eq. (4) which is the general expression for the normal energy distribution within the metal, applicable to any temperature. We again use Eq. (7), which states that only those electrons will be able to reach the collecting plate against a retarding potential V which come up to the surface within the metal with a normal energy ϵ_n greater than the critical value ϵ_{n_0}, where $\epsilon_{n_0} = W_a + Ve - h\nu$. The total number, N, of such electrons reaching unit area of the surface in unit time is given by

[10] E. U. Condon, Rev. Mod. Phys. **3**, 43 (1931).
[11] L. Nordheim, reference 9.

$$N=\int_{\epsilon_{n_0}}^{\infty} n(\epsilon_n)d\epsilon_n.$$

We will again assume that the number actually reaching the collector is proportional to N. If we write for brevity $W_a'=W_a+Ve$ and use the expression for $n(\epsilon_n)$ of Eq. (4) we have

$$F(V)=\beta(4\pi mkT/h^3)\int_{(Wa'-h\nu)}^{\infty} \times \log_e[1+\exp([\mu-\epsilon_n]/kT)]d\epsilon_n, \quad (11)$$

where β is a proportionality constant.

Now the above integral is precisely the one evaluated by Fowler[5] in computing the *total* number of electrons ejected by the frequency ν, except that in the lower limit W_a is replaced by W_a'. This is to be expected, since the effect of a uniform retarding field is simply to increase the effective potential barrier against which the electrons must escape. Fowler's result is, in our present notation,

$$F(V)=\beta\{2(2)^{\frac{1}{2}}\pi m^{\frac{1}{2}}k^2T^2/h^3[W_a'-h\nu]^{\frac{1}{2}}\}\Phi_1(x), \quad (12)$$

where

$$x=(h\nu-[W_a'-\mu])/kT$$
$$=(h\nu-[W_a+Ve-\mu])/kT=e(V_m-V)/kT, \quad (13)$$

and

$$\Phi_1(x)=e^x-e^{2x}/2^2+e^{3x}/3^2-\cdots \quad \text{for } x\leqq 0$$
$$=\pi^2/6+x^2/2-(e^{-x}-e^{-2x}/2^2+e^{-3x}/3^2-\cdots) \quad \text{for } x\geqq 0.$$

Eq. (12) for the voltage-current curve can be compared with experimental curves by a method similar to that used by Fowler. For this purpose the equation may be written in the form

$$\log(F/T^2)=B+\Phi(x). \quad (14)$$

where B is a constant and $\Phi(x)=\log_{10}\Phi_1(x)$. Now $\Phi(x)$ is a universal function of x, the form of the function being shown in Fig. 8 below. If the observed current-voltage curve is plotted in the form $\log(I/T^2)$ as a function of $(-Ve/kT)$ the resulting curve should be of the same shape as the theoretical curve, and should, after a shift parallel to itself, be superposable on it. The amount of the vertical shift is unimportant, depending on the constant B, the intensity of the light, and the units used. The horizontal shift, however, should be equal to eV_m/kT where $eV_m=h\nu-\phi e$, so that V_m is the maximum energy of emission which would be observed if the metal surface were at 0°K. If V_m is determined in this way for a series of frequencies the values should be found to fit the Einstein equation. This method of testing the equation is free from the uncertainty involved in an arbitrary extrapolation of an observed curve which really approaches the axis asymptotically.

4. Experimental test

Experiments are now being conducted by the writer, in collaboration with Dr. R. C. Hergenrother of this laboratory, to test the above theory. A detailed account of these experiments will be published in the near future, after more complete data have been obtained. The results obtained so far, however, furnish a convincing verification of the theory. The details of the experimental technique need not be described here. Suffice to say that the parallel-plate arrangement of the electrodes was used, the photoelectrons being ejected from a thoroughly outgassed strip of molybdenum. The collecting plate is of nickel, which when outgassed has a work function sufficiently high that it is photoelectrically insensitive to the wave-lengths used. The incident light is resolved by a Hilger monochromator with suitable filters to remove scattered light of short wave-length. While the apparatus is designed to allow measurements to be carried out at any temperature of the molybdenum, only the room temperature measurements have so far been completed.

The current-voltage curves, plotted in the usual way, for four different wave-lengths, are shown in Fig. 7. The portion of these curves in the vicinity of the saturation current is not of interest, since the theory does not apply to this portion and since experimentally it is distorted by reflected electrons. Therefore in the figure only the "tails" of the curves are shown, except that in the inset the complete curve for λ2536 is plotted. The portion of this curve plotted to the large scale below is that to the left of the line A. These curves show clearly the predicted asymptotic approach to the axis. The result of analyzing

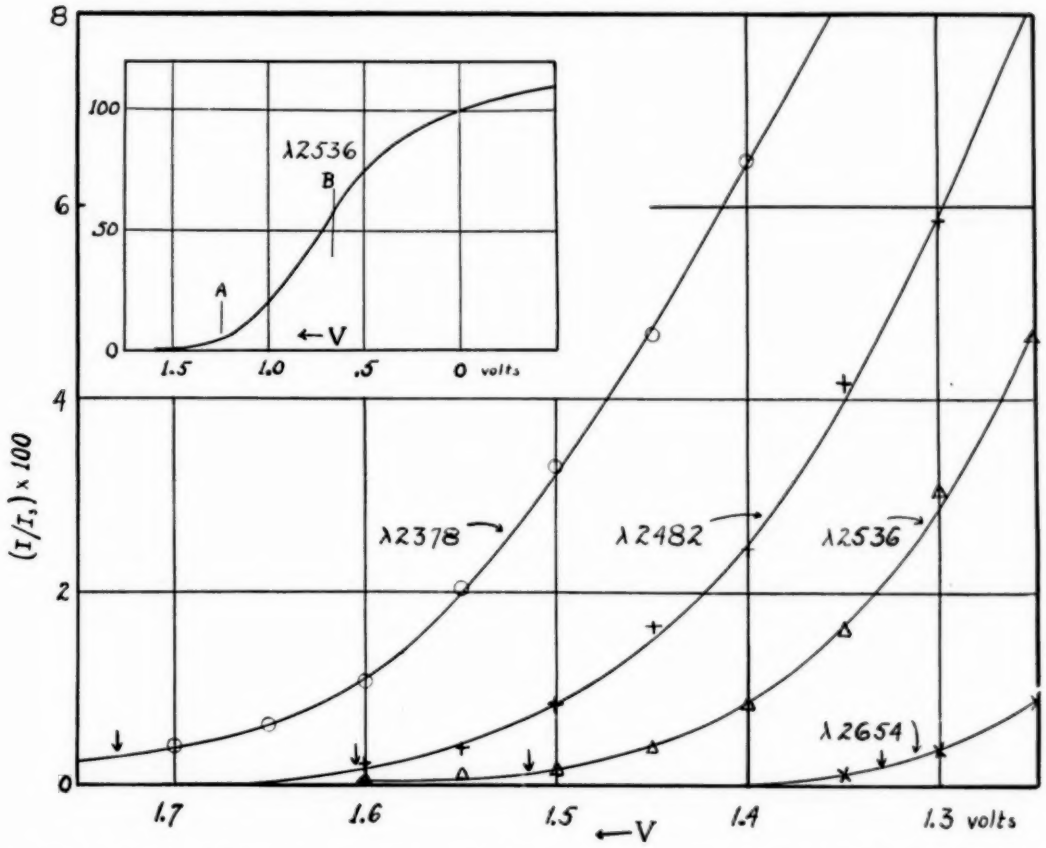

FIG. 7. Experimental current-voltage curves for Mo at room temperature, using parallel plate electrodes. Inset, complete curve for λ2536. Lower curves, magnified portion of the tail. I_s = saturation current. Arrows indicate values of V_m for 0°K.

these curves by the method outlined in the previous section is shown in Fig. 8. The full line is the theoretical curve, and the experimental points are shown after each observed curve has been shifted by the proper amount. The agreement with the theory is well within the limits of experimental error. The portion of the observed curve which can be made to fit the theoretical is roughly that to the left of line B in the inset of Fig. 7, so that the theory predicts the proper shape for the whole lower half of the curve.

From the horizontal shifts required to bring any experimental curve into coincidence with the theoretical, one can determine V_m, the maximum emission energy at 0°K, for that wave-length. The positions of the maximum energies so determined are indicated by the arrows in Fig. 7. If the curves in this figure were extrapolated in the usual way to determine V_m, values greater by several hundredths of a volt would be obtained. It is evident, therefore, that even at room temperature the thermal energies of the electrons are sufficiently important to introduce an uncertainty of this amount into the determination of V_m by the extrapolation method. The experiments have not as yet been carried to sufficient precision to allow an accurate determination of h/e. Nevertheless, the differences between the values of V_m for the different wave-lengths, as determined by the new method, agree roughly with the theoretical values predicted by the Einstein equation. Thus for the two lines 2482A and 2653A the difference between the values of V_m is 0.27 volt, while the corresponding value of $(h/e)(\nu_1-\nu_2)$ is 0.32 volt. The difference can undoubtedly be traced to small changes in contact potential between the emitting and collecting surfaces.

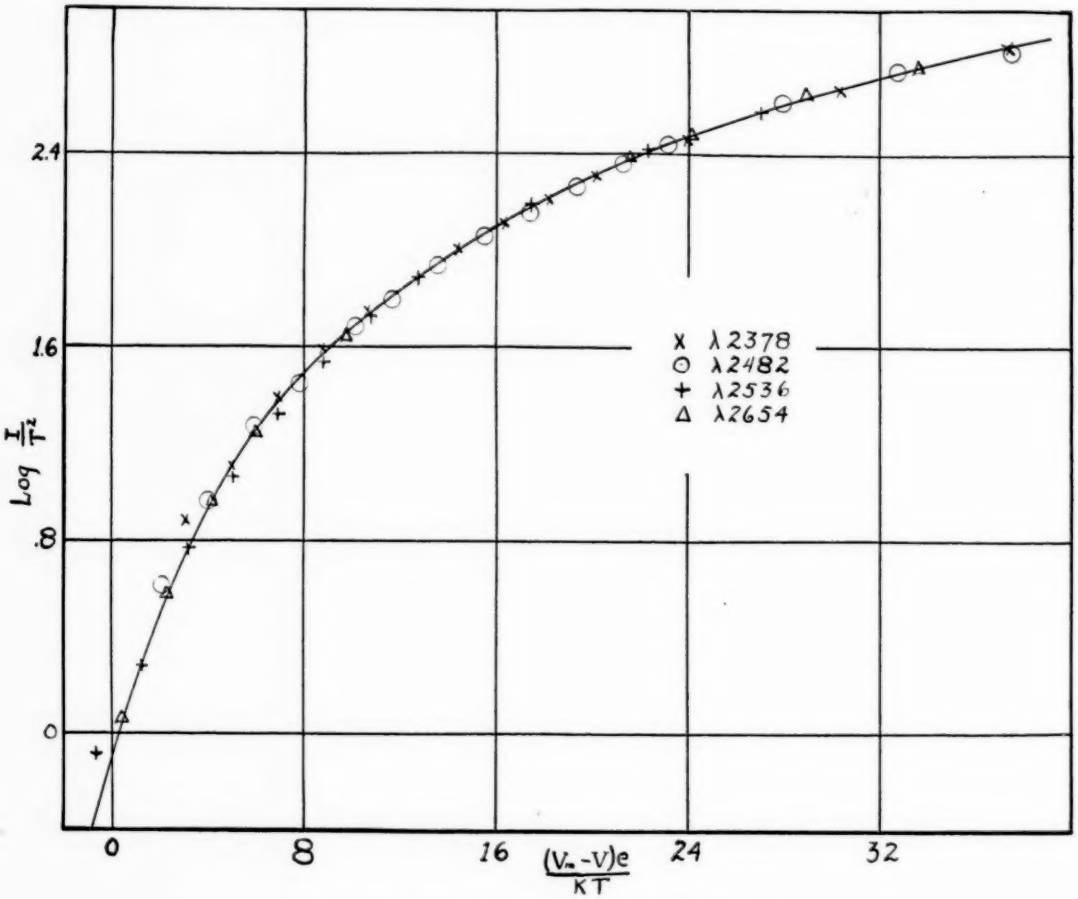

FIG. 8. Analysis of current-voltage curves for Mo.

II. DISTRIBUTION OF TOTAL ENERGIES

5. General statement

While it is possible to analyze the distribution of normal energies of photoelectrons by parallel plate electrodes, most experiments on energy distribution have made use of an arrangement in which the ability of an electron to reach the collecting electrode depended on its *total* energy rather than that normal to the surface. The ideal arrangement for accomplishing this is to have the photoelectrons ejected from a small sphere placed at the center of a much larger collecting sphere. It is desirable to deduce an equation for the energy distribution and voltage current curves to be expected in this case. To do this we will make use of assumptions analogous to those used in Part I and use the following notation:

Let the original velocity of an electron within the metal be u_0, whose rectangular components are ξ_0, η_0, ζ_0, where ξ_0 is chosen normal to the illuminated surface. Calling the corresponding energy ϵ_0, we have

$$\epsilon_0 = \tfrac{1}{2}mu_0^2 = \tfrac{1}{2}m(\xi_0^2+\eta_0^2+\zeta_0^2). \quad (15)$$

If the electron absorbs a quantum $h\nu$ it will attain an energy ϵ and a corresponding velocity u with components ξ, η, ζ, such that

$$\epsilon = \tfrac{1}{2}mu^2 = \tfrac{1}{2}m(\xi^2+\eta^2+\zeta^2) = \tfrac{1}{2}mu_0^2+h\nu. \quad (16)$$

If such an electron comes up to the surface with a velocity u whose component perpendicular to the surface ξ is greater than some critical value ξ_c, where $\frac{1}{2}m\xi_c^2 = W_a$, the electron may escape from the surface with the energy loss W_a. Let v be the total velocity of escape and E the corresponding energy; and call the component of v normal to the surface v_n. Then we will have

$$E = \tfrac{1}{2}mv^2 = \tfrac{1}{2}mu^2 - W_a = \tfrac{1}{2}m(u^2-\xi_c^2) \quad (17)$$

and

$$\tfrac{1}{2}mv_n^2=\tfrac{1}{2}m(\xi^2-\xi_c^2). \tag{18}$$

At the absolute zero the maximum energy with which an electron can come up to the surface is $(\mu+h\nu)$. Hence the maximum velocity of escape, v_m, and the corresponding maximum energy E_m will be given by the Einstein equation, as before,

$$\tfrac{1}{2}mv_m^2=E_m=h\nu-(W_a-\mu). \tag{19}$$

Since we will be continually using the Fermi-Dirac distribution function it will be convenient to make the following abbreviations: Let

$$\Psi(u_0)=\frac{1}{e^{(\frac{1}{2}mu_0^2-\mu)/kT}+1}. \tag{20}$$

Substituting for u_0 its value in terms of u from Eq. (16) we have

$$\Psi(u)=\frac{1}{e^{(\frac{1}{2}mu^2-h\nu-\mu)/kT}+1}. \tag{21}$$

Or finally in terms of v, from Eq. (17),

$$\Psi(v)=\frac{1}{e^{(\frac{1}{2}mv^2+W_a-h\nu-\mu)/kT}+1} \tag{22}$$

$$=\frac{1}{e^{(E-E_m)/kT}+1}.$$

6. General equation for energy distribution

The number of electrons per unit volume within the metal having total velocities between u_0 and u_0+du_0 is given by the Fermi-Dirac function

$$n(u_0)du_0=(8\pi m^3/h^3)u_0^2\Psi(u_0)du_0, \tag{23}$$

where $\Psi(u_0)$ is defined by Eq. (20). When the surface is illuminated a certain fraction, p, of these electrons will absorb the energy $h\nu$ attaining thereby the velocity u in the range du, where,

$$u^2=u_0^2+2h\nu/m,$$

and hence

$$udu=u_0du_0.$$

The number of electrons per unit volume having the velocity u in the range du will then be

$$n(u)du=(8\pi m^3/h^3)p[u^2-(2h\nu/m)]^{\frac{1}{2}}u\Psi(u)du. \tag{24}$$

Of these electrons only those can escape which have velocity components normal to the surface greater than the critical value ξ_c defined above. But since the velocities are equally distributed in all directions, it can readily be shown that the fraction of the total number of electrons having the velocity u, whose velocities are directed in such a way that the component normal to the surface is equal to or greater than ξ_c is $\frac{1}{2}(1-\xi_c/u)$. If we multiply $n(u)$ by this factor, and also by ξ, we get the number coming up to unit area of the surface per second with energies sufficient to escape. Multiplying then by the transmission coefficient $D(u)$, we get the number actually escaping. Now electrons which come up to the surface with the velocity u in the range du and escape will emerge with the velocity v in the range dv, and from Eq. (17) we have

$$v^2=u^2-\xi_c^2$$

$$vdv=udu.$$

Hence the number escaping per second with velocities in the range between v and $v+dv$ is given finally by

$$N(v)dv=(8\pi m^3/h^3)p\xi D(v)[v^2+\xi_c^2-2h\nu/m]^{\frac{1}{2}}\cdot\tfrac{1}{2}[1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]v\Psi(v)dv, \tag{25}$$

where $\Psi(v)$ is defined by Eq. (22).

Eq. (25) is the general equation for the *velocity* distribution of the emitted electrons, in which no approximations have been made. The equation can be greatly simplified by making approximations of the same order as in Part I. This involves assuming that the factor p is constant and that $D(v)=1$. In addition, if ν is not too far from the threshold ν_0, the factor ξ will not differ greatly from ξ_c and hence may be assumed constant. Also we will have $u^2=(v^2+\xi_c^2)\gg 2h\nu/m$, so that the first factor in the brackets may be expanded and second order terms neglected, giving,

---

$$[(v^2+\xi_c^2)-2h\nu/m]^{\frac{1}{2}}=(v^2+\xi_c^2)^{\frac{1}{2}}-[h\nu/m(v^2+\xi_c^2)^{\frac{1}{2}}].$$

Now this is to be multiplied by the second factor in brackets. The first term of the product may be expanded as follows:

$$(v^2+\xi_c^2)^{\frac{1}{2}}[1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]=(v^2+\xi_c^2)^{\frac{1}{2}}-\xi_c=v^2/2\xi_c=\alpha v^2,$$

since $v^2 \ll \xi_c^2$, α being a constant $=1/2\xi_c$. The second term gives, similarly,

$$[h\nu/m(v^2+\xi_c^2)^{\frac{1}{2}}][1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]=[h\nu/m(v^2+\xi_c^2)](v^2/2\xi_c)=\beta v^2,$$

where β, the coefficient of v^2, can be considered essentially constant, since $v^2 \ll \xi_c^2$ and only small ranges of v are to be considered. Making use of the above results, and of Eq. (22), we have finally from Eq. (25)

$$N(v)dv=A''\frac{v^3dv}{e^{(E-E_m)/kT}+1}. \tag{26}$$

$$A''=\text{const.},$$

as our final equation for the *velocity* distribution. Making now the substitutions $V'e=(\frac{1}{2})mv^2$ and $edV'=mvdv$ we have for the *energy* distribution function

$$f(V')dV'=A\frac{V'dV'}{e^{(V'-V_m)e/kT}+1}, \tag{27}$$

where $A=A''\cdot 2e^2/m^2$.

In Fig. 9, $f(V')$ is plotted as a function of V' for the temperatures 0°, 300° and 900°K and

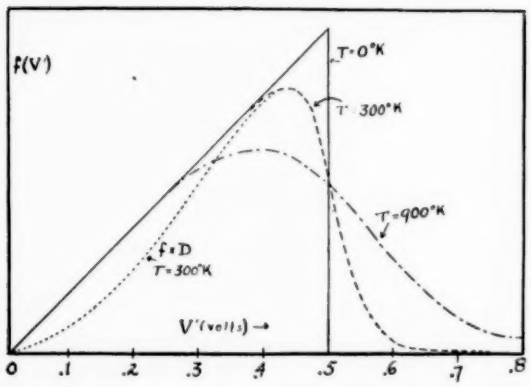

FIG. 9. Theoretical distribution of total energies for three temperatures.

for $V_m=0.5$ volt. It is seen that the sharpness of the "maximum" energy is greatly affected by the temperature. It has been occasionally suggested that the "apparent" maximum energy, determined by an arbitrary extrapolation of a room temperature curve, would be the same as the true maximum energy for 0°K. The curves show, however, that this is far from being the case. It is evident also that the form of the curves is not that usually obtained experimentally. If one corrects, as before, for the variation of the transmission coefficient D, a distribution curve of the form shown by the dotted curve is obtained, which resembles more nearly the experimental curve. However, even with this correction the most probable energy on the theoretical curve is much nearer the "maximum" energy than in most experimental curves. Experiments are now in progress in this laboratory to test the cause of this discrepancy. Some experiments of Bennewitz[12] suggest that the most probable energy shifts to higher values as the surface is outgassed, and our preliminary results show that the curves for *very clean* surfaces more nearly resemble the theoretical curves.[13]

In order to make direct comparison with experiment, however, it is desirable to obtain an expression for the current-voltage curve, in order to eliminate the uncertainties involved in differentiating an experimental curve.

7. Current-voltage curve

If the collecting sphere is at a potential V, negative to the emitting surface, the number of electrons received will be the total number emerging from the surface with energies greater than Ve. Hence

$$F(V)=\int_V^\infty f(V')dV'$$

$$=\int_V^\infty \frac{AV'dV'}{e^{(V'-V_m)e/kT}+1}. \tag{28}$$

This integral may be evaluated by making the substitutions:

$$x=Ve/kT, \quad x'=V'e/kT, \quad dx'=edV'/kT,$$

$$\text{and} \quad x_0=V_me/kT.$$

[12] W. Bennewitz, Ann. d. Physik **83**, 913 (1927).

[13] It should be pointed out that the form of the theoretical curve is similar to that deduced by Fröhlich (Ann. d. Physik **7**, 103 (1930)) for the case of thin films.

Then

$$F(V)=Ak^2T^2\int_x^\infty \frac{x'dx'}{e^{(x'-x_0)}+1}. \tag{29}$$

By making the further substitutions $e^{x'}=w$, $dx'=dw/w$, and $e^{-x_0}=a$, the integral becomes

$$\int \frac{\log w\, dw}{w(aw+1)}. \tag{30}$$

This may be integrated by parts by using standard forms. The form of the result depends on whether x' is greater or less than x_0, so that for the value of the indefinite integral (30) we find

$$F_1=x'(x'-x_0)-\tfrac{1}{2}(x'-x_0)^2-x'\log\left[1+e^{(x'-x_0)}\right]+\left[e^{(x'-x_0)}-e^{2(x'-x_0)}/2^2+e^{3(x'-x_0)}/3^2-\cdots\right], \quad \text{for } x'\leqq x_0.$$

$$F_2=x'(x'-x_0)-x'\log\left[1+e^{(x'-x_0)}\right]-\left[e^{-(x'-x_0)}-e^{-2(x'-x_0)}/2^2+e^{-3(x'-x_0)}/3^2-\cdots\right], \quad \text{for } x'\geqq x_0.$$

In case the applied retarding potential V is less than V_m (i.e., $x<x_0$) we substitute the limits x to x_0 in F_1 and x_0 to ∞ in F_2, then

$$F(V)=Ak^2T^2\{[F_1]_x^{x_0}+[F_2]_{x_0}^{\infty}\}, \quad x\leqq x_0.$$

In case $V>V_m$, i.e., $x>x_0$, we have

$$F(V)=Ak^2T^2[F_2]_x^{\infty}, \quad x\geqq x_0.$$

Substitution of the limits gives

$$F(V)=Ak^2T^2\{\pi^2/6-\tfrac{1}{2}(x^2-x_0^2)+x\log\left[1+e^{(x-x_0)}\right]-\left[e^{(x-x_0)}-(1/2^2)e^{2(x-x_0)}+(1/3^2)e^{3(x-x_0)}-\cdots\right]\}, \quad x\leqq x_0 \tag{31}$$

$$F(V)=Ak^2T^2\{-x(x-x_0)+x\log\left[1+e^{(x-x_0)}\right]+\left[e^{-(x-x_0)}-(1/2^2)e^{-2(x-x_0)}+(1/3^2)e^{-3(x-x_0)}-\cdots\right]\}, \quad x\geqq x_0. \tag{32}$$

For the case $V=V_m$ (i.e., $x=x_0$) either of the above expressions reduces to

$$F(V_m)=Ak^2T^2(x_0\log 2+\pi^2/12), \quad x=x_0.$$

Eqs. (31) and (32) are the final equations for the current voltage curves for the case of spherical electrodes. Before discussing them in detail it is of interest to consider two limiting cases.

(1) For $T=0°\mathrm{K}$ the equations become, on setting $x=Ve/kT$ and $x_0=V_me/kT$,

$$\begin{aligned} F_0(V)&=(Ae^2/2)(V_m^2-V^2) && \text{for } V\leqq V_m \\ F_0(V)&=0 && \text{for } V\geqq V_m. \end{aligned} \tag{33}$$

The current voltage curve at absolute zero is thus a parabola, and there is a sharply defined maximum retarding potential.

(2) For $V=0$, i.e., no retarding potential, $F(V)$ should be equal to the total saturation current. Setting $x=0$ in Eq. (31), we have

$$F(0)=Ak^2T^2\{\pi^2/6+x_0^2/2-\left[e^{-x_0}-e^{-2x_0}/2^2+e^{-3x_0}/3^2-\cdots\right]\}. \tag{34}$$

Remembering that $x_0=V_me/kT=(h\nu-\phi e)/kT=h(\nu-\nu_0)/kT$, this equation is found to be identical with that obtained by Fowler for the total number of electrons ejected from a surface at the temperature T by the frequency ν which is greater than the threshold ν_0. This agreement is to be expected, since the approximations used in the present analysis are of the same order as those employed by Fowler.

It is seen from Eqs. (31) and (32) that $F(V)$ is not a universal function of V as in the case considered in Part I. The form of the curve obtained depends on the absolute value of x_0 $[=h(\nu-\nu_0)/kT]$. That is, for a given temperature the form of the curve will depend on the difference between the incident frequency and the threshold frequency for the particular surface. Or, for a given value of $(\nu-\nu_0)$, or of V_m, the form of the curve depends on the temperature. These effects are seen in Fig. 10, where relative values of $F(V)$ are plotted as a function of x/x_0 for several values of x_0. The curve for $x_0=\infty$ would be obtained at $0°\mathrm{K}$ for any incident

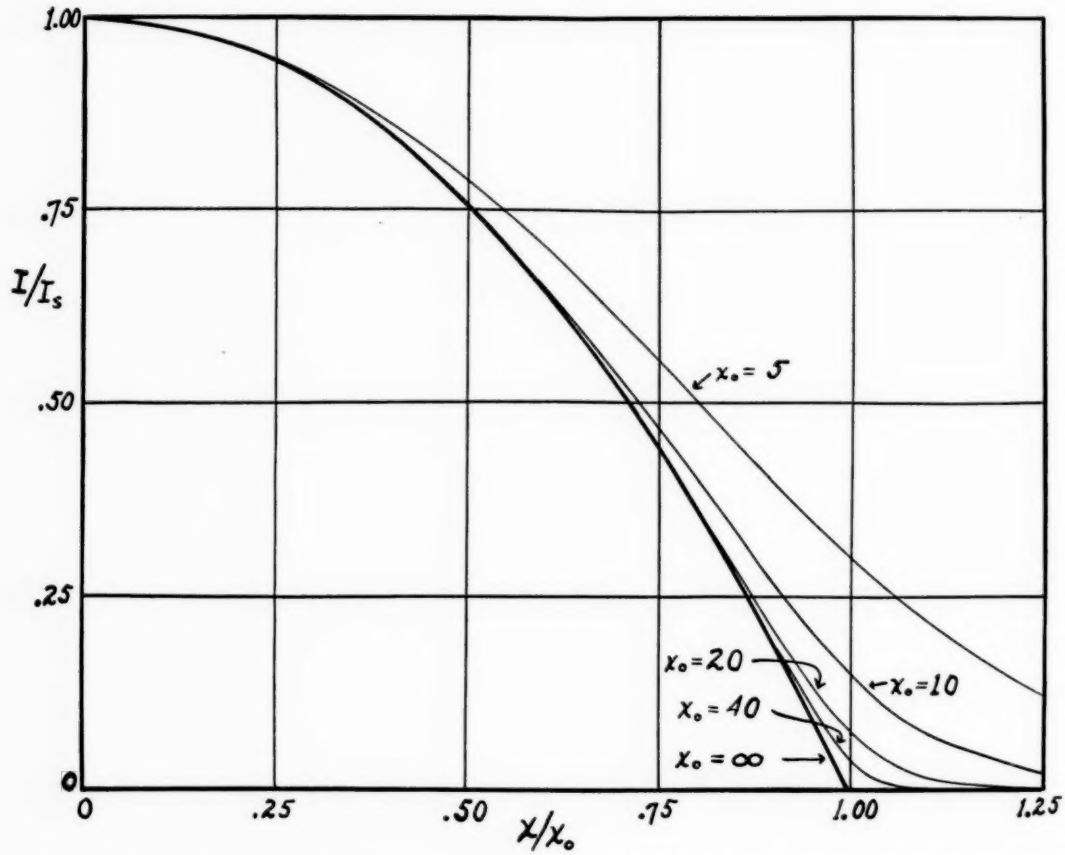

FIG. 10. Theoretical current-voltage curves for various values of x_0, reduced to the same saturation current, I_s.

frequency. It is the parabola given by Eq. (33). For $T=300°\text{K}$ the different curves would correspond to values of V_m as follows:

x_0	∞	40	20	10	5
V_m (volts)	∞	1.04	0.52	0.26	0.13

On the other hand, if the incident frequency were chosen so that $V_m=0.5$ volt, for example, the temperatures corresponding to the various curves would be:

x_0	∞	40	20	10	5
$T°\text{K}$	0	150	300	600	1200

Although the calculation of a complete $F(V)$ curve from Eqs. (31) and (32) is somewhat tedious, the process is greatly simplified by using the following approximations, which are valid for the regions indicated:

$$F(V)=\tfrac{1}{2}Ak^2T^2[(x_0^2-x^2)+\pi^2/3], \quad \text{for } (x_0-x)>3 \quad (35)$$

$$=Ak^2T^2(x_0\log 2+\pi^2/12), \quad \text{for } (x_0-x)=0$$

$$=Ak^2T^2\{x[e^{-(x-x_0)}-(1/4)e^{-2(x-x_0)}]\}, \quad \text{for } (x_0-x)<-1 \text{ and } x_0>10. \quad (36)$$

Eq. (36) above is not easily deduced analytically, but it was found accidentally in numerical calculation to hold very closely.

8. Experimental test

An experimental test of this portion of the theory is being carried out in this laboratory by Mr. W. W. Roehr, whose results will be published in a later paper. The results so far obtained, however, are again in excellent agreement with the theory.

The experimental set-up in this case is designed to approximate as closely as possible the ideal concentric-sphere arrangement. Photoelectrons are liberated from a small strip of thoroughly

outgassed molybdenum placed at the center of a large collecting sphere. The incident light is resolved by a double quartz monochromatic illuminator which eliminates scattered light of short wave-lengths. Again the apparatus is designed to take measurements at any temperature of the molybdenum, though at present only the room temperature measurements have been completed.

In analyzing these results a somewhat different graphical method has been developed. Referring to Eq. (36), it is seen that the expression for the tail of the theoretical curve (i.e., $x>x_0$) may be written approximately in the form

$$F(V)=Ak^2T^2xf(x-x_0),$$

where $f(x-x_0)$ is a universal function of its argument. This equation may be rewritten in the form

$$\log\,(F/xT^2)=B+f'(x-x_0),$$

where $f'=\log f$. Plotting f' as a function of (x_0-x) gives the curve shown in Fig. 11. If the experimental results are then plotted in the form $\log\,(I/xT^2)$ as a function of x (or, at a fixed temperature, $1/T^2$ may be absorbed in the constant B) the curve obtained should be of the same form as the theoretical curve and, after a shift parallel to itself, should be superposable on it. The amount of the horizontal shift again determines x_0, and hence V_m as before. The results of analyzing the experiments in this way are shown in Fig. 11. Again it is seen that at room temperature the shape of the lower portion of the experimental curve is very closely that predicted by the theory. The complete current-voltage curves, plotted in the usual way, are shown in Fig. 12, with the values of V_m obtained as above indicated by arrows. The difference between the values of V_m for the lines 2536A and 2804A is 0.50 volt, and the corresponding value of $(h/e)(\nu_1-\nu_2)$ is 0.49 volt, the agreement being within the limit of error of the observations. The form of the theoretical curve for 0°K is indicated approximately by the broken lines in Fig. 12. It is seen that in this case the temperature tail gives rise to a considerable uncertainty in the determination of V_m by the extrapolation method.

9. Conclusion

While the verification of the theory presented in this paper will not be complete until the more extended and more accurate measurements now under way in this laboratory are finished, the preliminary results indicate that the theory predicts the correct form of the energy distribution and current-voltage curves in the vicinity of the maximum energy. Aside from giving for the first time a quantitative expression for the form of these curves, one of the chief points of interest in the theory is that it brings out clearly the uncertainty in any determination at ordinary temperatures of the "maximum" emission energy of photoelectrons by the usual extrapolation methods. At the same time it yields a method for determining the true maximum energy at 0°K.

This raises the question as to how it happens that the photoelectric method of determining h (involving an arbitrary extrapolation) has yielded such accurate results in the past. Referring first to the experiments in which the alkali metals were used, such as those of Millikan[3] and of Olpin,[14] the reason for their success can be seen from an examination of the curves of Fig. 10. With alkali metals the value of $(\nu-\nu_0)$, and hence of x_0, may be quite large, up to about 3 volts. The theoretical curve for this case $(x_0\sim 120)$ would practically coincide with the curve labelled $x_0=\infty$, the temperature tail being probably too small to be observed, or at least small enough to be neglected when the extrapolation is made.[15] Hence in this case the extrapolation method would yield practically the value of V_m which would be observed at absolute zero. Millikan purposely ignored the rather large tails to some of his curves, attributing them to the presence of scattered light of short wavelength. While most of the tail was proably due to this cause, this method certainly ignored also a small tail due to thermal energies. The fact that Millikan's experiments yielded the correct value of h while the previous experiments of Hughes[2] and Richardson and Compton[1] did not, may be due in part to the fact that in the latter

[14] A. R. Olpin, Phys. Rev. **36**, 251 (1930).

[15] In the case of the alkali metals also it is no longer true that $\frac{1}{2}mu^2>>h\nu$ and some of the approximations made in the theory would fail, so that the curves of Fig. 10 would have a different form.

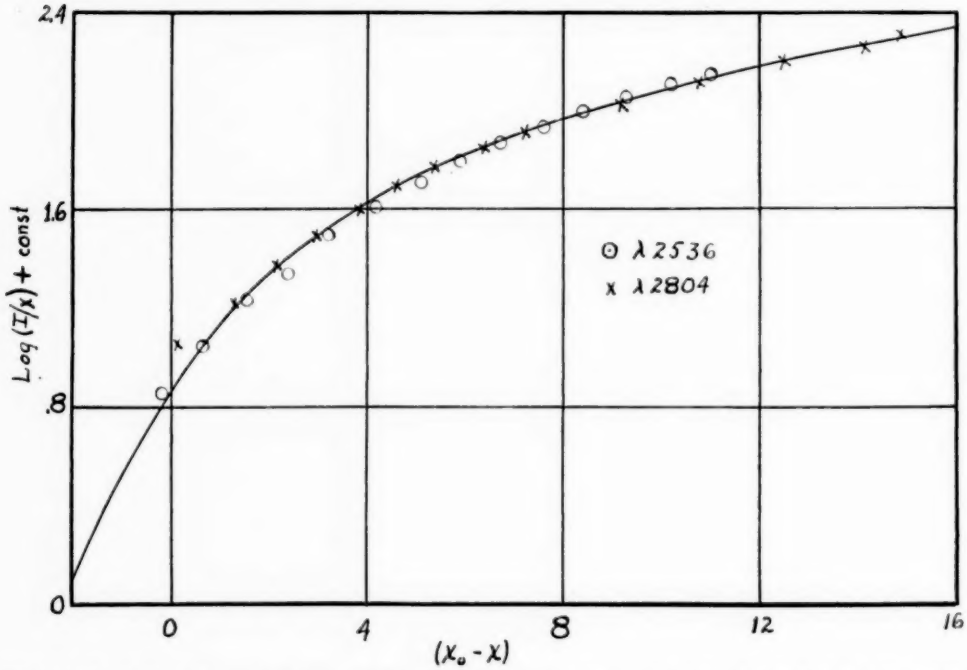

FIG. 11. Analysis of current-voltage curves for Mo at room temperature, using spherical electrodes.

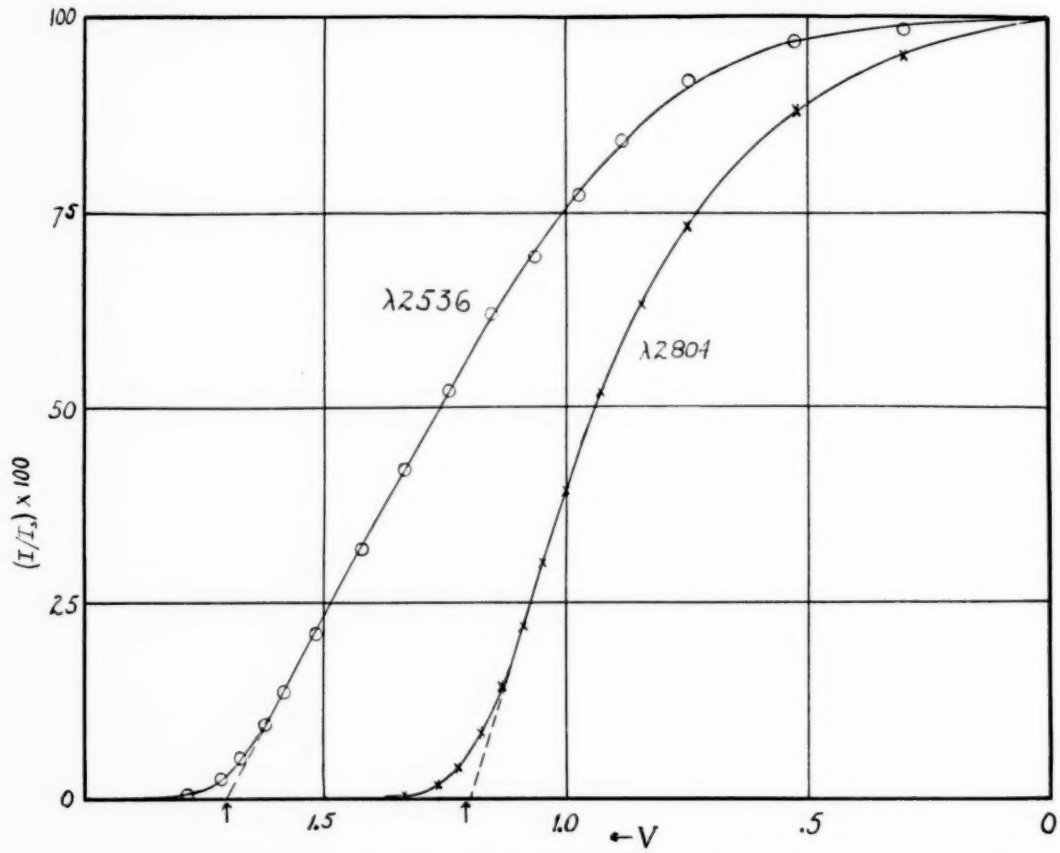

FIG. 12. Observed current-voltage curves for clean Mo. Broken lines indicate approximately the theoretical shape of the tail for 0°K. To avoid congestion only a few of the observed points are plotted.

experiments alkali metals were not used so that the values of $(\nu-\nu_0)$ were small, and hence the temperature effect relatively more important. In this case the extrapolation method fails.

It is more difficult to account for the amazing precision attained in the experiments of Lukirsky and Prilezaev[16] who employed metals such as silver, gold and platinum. For the values of $(\nu-\nu_0)$ which they used the effect of temperature on the tail of the curve is by no means negligible. At room temperature the values of V_m obtained by extrapolation would be from 5 to 25 percent greater than the value of V_m at 0°K. One must apparently assume that a fortunate method of extrapolation was chosen which happened to yield values of V_m which were always greater *by exactly the same amount* than the absolute zero values. This would yield a correct value of h. An alternative explanation may be sought in the fact that their experimental curves were not at all of the form of the theoretical curves of Fig. 10. The evidence at present suggests that this is due to the fact that they made no attempt to outgas the illuminated surfaces. The presence of gas in a surface might alter the form of the surface potential barrier or, more probably, affect the collision phenomena within the metal, in such a way that the assumptions made in our theory no longer apply. This might alter the shape of the current-voltage curve so as to make the temperature effect relatively less important. Even in this case, however, it is very difficult to understand how values of V_m *consistent among themselves to 0.001 volt* (as is claimed) could be obtained except as a result of an exceedingly fortuitous extrapolation method.

In conclusion the author wishes to express his indebtedness to Dr. R. C. Hergenrother and Mr. W. W. Roehr who have carried out the experimental work described here, and to acknowledge that this work was made possible through an appropriation to the author from a grant made by the Rockefeller Foundation to Washington University for research in science.

[16] P. Lukirsky and S. Prilezaev, Zeits. f. Physik **49**, 236 (1928).

An Extension of the Pd I-Like Isoelectronic Sequence to Antimony VI and Tellurium VII*

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(Received January 27, 1933)

With a vacuum spectrograph in the region 784 to 1331A some of the lines arising from the transition d^9p to d^9s electronic configurations of Sb VI and Te VII have been found. The wave-lengths and frequencies of the stronger lines are given along with the values for the sixteen terms $^3P^0D^0F^0$, $^1P^0D^0F^0(4d^95p)$ and ^3D, $^1D(4d^95s)$. Extrapolations were made from a Moseley diagram for the value of $^1S_0$, as the shorter wave-lengths (below 300A) for the $^1P_1^0$, $^3P_1^0$, and $^3D_1^0$ into $^1S_0$ were not obtained. Centroidal and fan type diagrams are also given.

THE terms and related wave-lengths and frequencies arising from the electronic configurations d^{10}, d^9s, d^9p have been previously identified for Pd I[1] and Ag II[2] by Shenstone, and for Cd III by McLennan, McLay and Crawford.[3] Cd III was also worked out by Gibbs and White,[4] who extended the isoelectronic sequence to In IV[4] and Sn V.[5] The present paper continues the extension to include Sb VI and Te VII.

The three strongest lines of the triplets $D-F,^0$ $D-D^0$, $D-P^0$ are shown in Fig. 1. The transitions $^1P_1^0$, $^3P_1^0$, and $^3D_1^0$ $(4d^95p)$ into $^1S_0$ $(4d^{10})$ should be at 289, 296, and 284A for Sb VI and at 240, 245, and 236A for Te VII, following extrapolations from the Moseley diagram, Fig. 2. As the spectrograph did not give satisfactory measurements below 300A these transitions were not obtained.

In 1928, having only the first members of any series, Gibbs and White made extrapolations from the known values of Ag I for Pd I by use of the relations for the elements in the first long

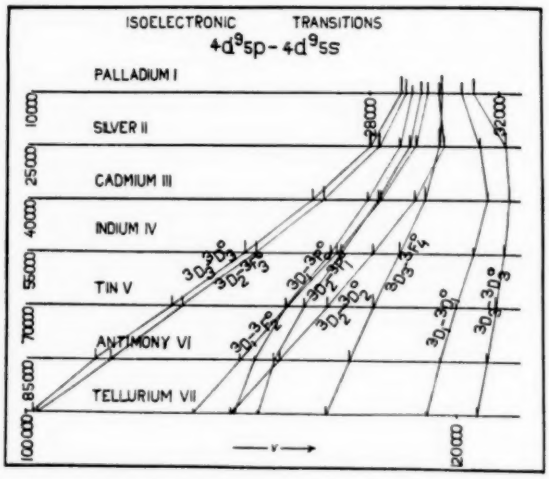

FIG. 1. Displacement of multiplets.

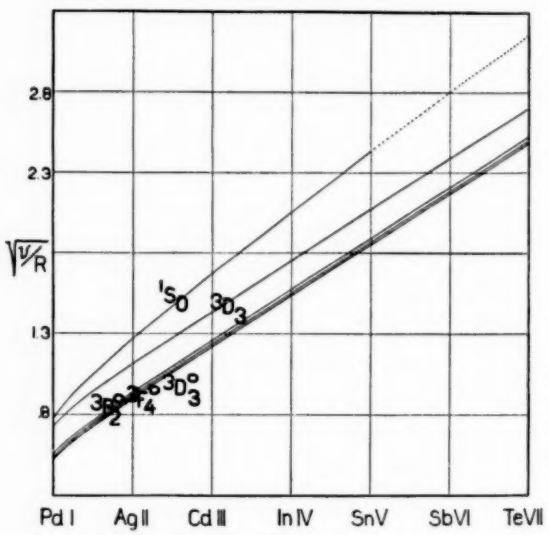

FIG. 2. Moseley diagram.

* Presented at the April, 1932, meeting of the American Physical Society in Washington.

[1] Pd I. Shenstone, Phys. Rev. **36**, 670 (1930).

[2] Ag II. Shenstone, Phys. Rev. **31**, 321 (1928). See also McLennan and Smith, Proc. Roy. Soc. Canada **20**, 110 (1926).

[3] Cd III. McLennan, McLay and Crawford, Trans. Roy. Soc. Canada **22**, 45 (1928).

[4] Cd III and In IV. Gibbs and White, Phys. Rev. **31**, 776 (1928).

[5] Sn V. Gibbs and White, Proc. Nat. Acad. Sci. **14**, 345 (1928).

TABLE I. *Values of* $(\nu/R)^{\frac{1}{2}}$.

Terms (Limit $4d^9$)		Pd I	Diff.	Ag II	Diff.	Cd III	Diff.	In IV	Diff.	Sn V	Diff.	Sb VI	Diff.	Te VII
$4d^{10}$	$^1S_0$	0.783	0.488	1.271	0.405	1.676	0.390	2.066	0.376	2.442	0.363	(2.805)	0.351	(3.156)
$4d^9 5s$	$^3D_3$	.731	.390	1.121	.320	1.441	.318	1.759	.315	2.074	.313	2.387	.310	2.697
$4d^9 5p$	$^3F_4^0$	.534	.389	0.923	.319	1.242	.318	1.560	.315	1.875	.313	2.188	.311	2.499
	$^3D_3^0$	.521	.388	.909	.319	1.228	.318	1.546	.316	1.862	.313	2.175	.312	2.487
	$^3P_2^0$	.550	.390	.940	.321	1.261	.320	1.581	.317	1.898	.313	2.212	.312	2.524

TABLE II. *Absolute values for lowest terms.*

	$4d^{10}$ $(^2D_{2\frac{1}{2}})$ $^1S_0$	Ionization potential
Pd I	67,236 cm^{-1}	8.3 volts
Ag II	177,164	21.8
Cd III	308,318	38.0
In IV	468,214	57.8
Sn V	654,527	80.7
Sb VI	(863,413)	(106)
Te VII	(1,093,017)	(135)

TABLE III. *Classified lines of Sb VI.*

λ (A)	ν (cm^{-1})	Int.	Designation	λ (A)	ν (cm^{-1})	Int.	Designation
? 883.45	113193	00	$^3D_2-{}^1D_2^0$	1035.85	96539.1	10	$^3D_2-{}^3P_1^0$
892.21	112081	3	$^3D_3-{}^1F_3^0$	1046.10	95593.2	2	$^3D_1-{}^3P_0^0$
? 897.35	111439	00	$^3D_2-{}^3D_1^0$	1051.39	95112.2	12	$^1D_2-{}^1P_1^0$
914.86	109306	5	$^3D_2-{}^1F_3^0$	1053.24	94945.1	20	$^3D_1-{}^3F_2^0$
940.26	106354	30	$^3D_3-{}^3D_3^0$	1072.94	93201.8	15	$^1D_2-{}^3D_3^0$
943.71	105964	5	$^3D_1-{}^1D_2^0$	1089.42	91791.8	00	$^1D_2-{}^3F_2^0$
952.96	104936	0	$^3D_3-{}^3F_3^0$	1090.36	91712.8	5	$^3D_3-{}^3F_3^0$
959.57	104213	5	$^3D_1-{}^3D_1^0$	1116.22	89588.1	3	$^3D_1-{}^3D_2^0$
972.66	102811	1	$^1D_2-{}^1D_2^0$	1119.63	89315.2	8	$^3D_1-{}^3P_1^0$
978.79	102167	5	$^3D_2-{}^3F_2^0$	1124.34	88941.1	25	$^3D_2-{}^3F_3^0$
? 989.52	101059	00	$^1D_2-{}^3D_1^0$	1133.20	88245.7	15	$^3D_3-{}^3P_2^0$
999.70	100030	35	$^3D_3-{}^3F_4^0$	1156.94	86434.9	10	$^1D_2-{}^3D_2^0$
1004.18	99583.7	5	$^3D_3-{}^3D_2^0$	1169.94	85474.5	5	$^3D_2-{}^3P_2^0$
1010.82	98929.6	2	$^1D_2-{}^1F_3^0$	1272.79	78567.6	20	$^1D_2-{}^3F_3^0$
1017.65	98265.6	5	$^3D_1-{}^1P_1^0$	1331.59	75098.2	1	$^1D_4-{}^3P_2^0$
1032.93	96812.0	20	$^3D_2-{}^3D_2^0$				

TABLE IV. *Classified lines of Te VII.*

λ (A)	ν (cm^{-1})	Int.	Designation	λ (A)	ν (cm^{-1})	Int.	Designation
784.09	127536	1	$^3D_3-{}^1F_3^0$	913.01	109528	20	$^3D_2-{}^3D_2^0$
803.56	124446	1	$^3D_2-{}^1F_3^0$	925.12	108094	0	$^1D_2-{}^1P_1^0$
827.06	120910	30	$^3D_3-{}^3D_3^0$	927.81	107781	7	$^3D_1-{}^3F_2^0$
829.84	120505	1	$^3D_1-{}^1D_2^0$	956.68	104528	0	$^1D_2-{}^3F_2^0$
843.21	118594	2	$^3D_1-{}^3D_1^0$	964.85	103643	0	$^3D_3-{}^3F_3^0$
852.87	117251	1	$^1D_2-{}^1D_2^0$	975.04	102505	8	$^3D_1-{}^3P_1^0$
? 861.60	116063	00	$^3D_2-{}^3F_2^0$	994.50	100553	10	$^3D_2-{}^3F_3^0$
866.99	115342	4	$^1D_2-{}^3D_1^0$	996.90	100311	25	$^3D_3-{}^3P_2^0$
877.59	113948	20	$^3D_3-{}^3F_4^0$	1007.54	99251.6	2	$^1D_2-{}^3P_1^0$
898.09	111347	1	$^3D_1-{}^1P_1^0$	1020.50	97991.2	0	$^1D_2-{}^3D_3^0$
902.63	110787	15	$^3D_2-{}^3P_1^0$	? 1028.61	97218.6	00	$^3D_2-{}^3P_2^0$
911.77	109677	1	$^3D_1-{}^3P_0^0$	1123.36	89018.6	15	$^1D_2-{}^3F_3^0$

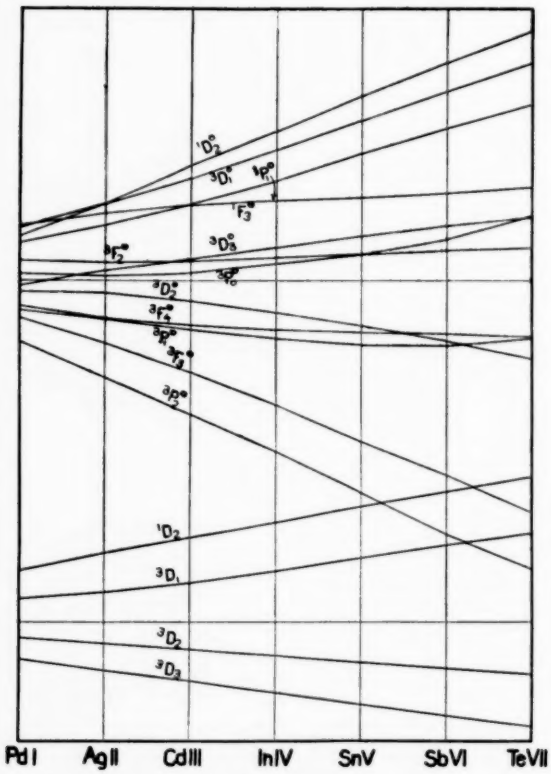

FIG. 3. Relative positions of the levels in each configuration.

period. Using the data for Pd I published in 1930 by Shenstone[1] and also the data for Ag II now available,[2] the author has remade the Moseley diagram of Gibbs and White and extended it to Sb VI and Te VII. In extrapolating the lines of this diagram beyond the first two elements, the term values have been so chosen as to make $\Delta(\nu/R)^{\frac{1}{2}}$ between terms that approach the same limit and arise from electronic configurations having the same total quantum number, remain constant. (See Table I.) The new absolute term values are about eight percent larger than those determined by the approximation by Gibbs and White. In Table II are given the absolute values of the lowest term with respect to $^2D_{2\frac{1}{2}}$, and the approximate ionization potentials. The smoothness of the curves in Fig. 1 and of the curves when the terms are plotted according to the centroids, Fig. 3, were of aid in selecting the proper lines.

TABLE V. *Term values.*

Designation	Sb VI	Te VII
$4d^95s\ ^3D_3$	0	0
$^3D_2$	2,771	3,090
$^3D_1$	9,994	11,372
$^1D_2$	13,147	14,625
$4d^95p\ ^3P_2^0$	88,246	100.311
$^3F_3^0$	91,713	103,643
$^3P_1^0$	99,311	113,877
$^3D_2^0$	99,583	112,617
$^3F_4^0$	100,030	113,948
$^3F_2^0$	104,939	119,153
$^3P_0^0$	105,587	121,049
$^3D_3^0$	106,354	120,910
$^1P_1^0$	108,259	122,719
$^1F_3^0$	112,077	127,536
$^3D_1^0$	114,207	129,966
$^1D_2^0$	115,954	131,877

The author wishes to thank Professor R. C. Gibbs, who suggested the extension of this isoelectronic sequence and who made possible the use of the vacuum spectrograph. An investigation recently completed extends a similar sequence ($5d^96p$) into ($5d^86s$) starting with Pt I to Bi VI, and the data for this sequence and for the sequence discussed in this paper were compared at the December, 1932, meeting of the American Physical Society in Atlantic City.

Multiplets in the Spectra of Cb III and Mo IV

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Additional multiplets in the three electron systems of Cb III and Mo IV.—The Moseley law and, one of its consequences, the irregular doublet law are applied to the known data for the triads of quartets $^4FD^0$, $^4FF^0$, FG^0 ($4d^3-4d^25p$) and $^4FD^0$, $^4FF^0$, $^4FG^0$ ($4d^25s-4d^25p$) in Yt I and Zr II to predict the position of the corresponding multiplets in Cb III and Mo IV. Nearly all of the terms in these two triads have been identified. Absolute term values for Cb III differ from those previously given. The lines were photographed with a 3 meter concave grating, first mounted for normal incidence and later for grazing incidence.

IT is well known that x-ray doublet laws have been successfully applied to optical spectra and are especially useful in predicting the positions of multiplets in complex spectra. The irregular doublet law, one of the consequences of the Moseley law, predicts a linear progression of the frequency with atomic number in an iso electronic sequence whenever the electron transitions involve only a change in the azimuthal quantum number. This linearity is shown in a paper by Gibbs and White[1] for the transitions $^4FG^0$, $^4FF^0$ and $^4FD^0$ ($4d^25s-4d^25p$) in the sequence Yt I, Zr II and Cb III.

A Moseley diagram constructed from the known term values in Yt I[2] and Zr II[3] predicts the normal electron configuration of Cb III and Mo IV to be $4d^3$. Of the many terms arising from this $4d^3$ configuration Hund's rule, when applied to this case, would indicate that the ^4F term should lie deepest and that $^4F_{1\frac{1}{2}}$ should be the normal state. The triad of quartet terms $^4D^0$, $^4F^0$, $^4G^0$, arising from the $4d^25p$ configuration, previously identified by Gibbs and White, should combine with this low ^4F term giving rise to very strong lines in the region of λ1500A. Most of the lines corresponding to these transitions have been photographed with a 3 meter concave grating mounted for normal incidence and are listed in Table II. Term values are given in Table I.

Extrapolating by means of the irregular doublet law, the triad of quartets $^4FD^0$, $^4FF^0$ and $^4FG^0$ ($4d^25s-4d^25p$) in Mo IV has been located in the region of λ 2000A. The identification was greatly facilitated by observing the similarity of the lower set of multiplets $^4FD^0$, $^4FF^0$ and $^4FG^0$ ($4d^3-4d^25p$) in Mo IV with those in Cb III located by means of extending the Moseley

TABLE I. *Term values in Cb III.*

Electron configuration	Term designation	Term values	Absolute term values	Electron configuration	Term designation	Term values	Absolute term values
	$a^4F_{1\frac{1}{2}}$	00.0	227004.9		$z^4G_{2\frac{1}{2}}^0$	63687.4	163317.5
$4d^3$	$a^4F_{2\frac{1}{2}}$	516.9	226488.0		$z^4G_{3\frac{1}{2}}^0$	65007.1	161997.8
	$a^4F_{3\frac{1}{2}}$	1176.6	225828.3		$z^4G_{4\frac{1}{2}}^0$	66456.5	160548.4
	$a^4F_{4\frac{1}{2}}$	1939.3	225065.6		$y^4F_{2\frac{1}{2}}^0$	67095.1	159909.8
					$y^4F_{3\frac{1}{2}}^0$	67868.7	159136.2
	$b^4F_{1\frac{1}{2}}$	25221.2	201783.7		$z^4G_{5\frac{1}{2}}^0$	68061.7	158943.2
$4d^25s$	$b^4F_{2\frac{1}{2}}$	25736.5	201268.4	$4d^25p$	$y^4F_{4\frac{1}{2}}^0$	68787.8	158217.1
	$b^4F_{3\frac{1}{2}}$	26464.9	200540.0		$x^4D_{0\frac{1}{2}}^0$	69184.2	157820.7
	$b^4F_{4\frac{1}{2}}$	27374.7	199630.2		$x^4D_{1\frac{1}{2}}^0$	69674.3	157330.6
					$x^4D_{2\frac{1}{2}}^0$	70280.7	156724.2
					$x^4D_{3\frac{1}{2}}^0$	70588.0	156416.9

[1] R. C. Gibbs and H. E. White, Phys. Rev. **31**, 520 (1928).

[2] William F. Meggers and Henry Norris Russell, Bur. Standards J. Research **2**, 55 (1929).

[3] C. C. Kiess and Harriet K. Kiess, Bur. Standards J. Research **5**, 255 (1930).

TABLE II. *Identified lines in Cb III.*

Relative intensity	λ (vac.)	ν	Designation	Mult. No.	Relative intensity	λ (vac.)	ν	Designation	Mult. No.
3	1599.72	62510.8	$a^4F_{3\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	100	1495.92	66848.5	$a^4F_{4\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	2
tr.	1585.60	63067.8	$a^4F_{4\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	3	1490.42	67095.1	$a^4F_{1\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	2
2	1583.02	63170.5	$a^4F_{2\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	10	1484.74	67351.8	$a^4F_{2\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2
5	1570.17	63687.4	$a^4F_{1\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	3	1479.04	67611.2	$a^4F_{3\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	2
3	1566.65	63830.5	$a^4F_{3\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	50	1456.69	68648.7	$a^4F_{4\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3
10	1550.62	64490.2	$a^4F_{2\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	30	1447.09	69104.1	$a^4F_{3\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	3
2	1549.97	64517.2	$a^4F_{4\frac{1}{2}}-z^4G_{4\frac{1}{2}}^0$	1	20	1445.98	69157.4	$a^4F_{2\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	3
15	1531.87	65279.9	$a^4F_{3\frac{1}{2}}-z^4G_{4\frac{1}{2}}^0$	1	15	1445.42	69184.2	$a^4F_{1\frac{1}{2}}-x^4D_{0\frac{1}{2}}^0$	3
3	1517.02	65918.5	$a^4F_{3\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	2	3	1440.69	69411.4	$a^4F_{3\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3
3	1516.77	65929.4	$a^4F_{4\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2	5	1435.25	69674.3	$a^4F_{1\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	3
10	1512.35	66122.4	$a^4F_{4\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	5	1433.41	69763.8	$a^4F_{2\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	3
40	1501.99	66578.2	$a^4F_{2\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	2	2	1427.12	70071.1	$a^4F_{2\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3
80	1499.43	66692.1	$a^4F_{3\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2	tr.	1422.87	70280.7	$a^4F_{1\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	3

TABLE III. *Term values in Mo IV.*

Electron configuration	Term designation	Term values	Absolute term values	Electron configuration	Term designation	Term values	Absolute term values
	$a^4F_{1\frac{1}{2}}$	0.0	374180.2		$z^4G_{2\frac{1}{2}}^0$	109412.9	264767.3
$4d^3$	$a^4F_{2\frac{1}{2}}$	780.0	373400.2		$z^4G_{3\frac{1}{2}}^0$	111336.6	262843.6
	$a^4F_{3\frac{1}{2}}$	1759.0	372421.2		$y^4F_{1\frac{1}{2}}^0$	111756.5	262423.7
	$a^4F_{4\frac{1}{2}}$	2858.6	371321.6		$y^4F_{2\frac{1}{2}}^0$	112921.0	261259.2
					$z^4G_{4\frac{1}{2}}^0$	113439.3	260740.9
	$b^4F_{1\frac{1}{2}}$	60893.4	313286.8	$4d^25p$	$y^4F_{3\frac{1}{2}}^0$	114619.4	259560.8
$4d^25s$	$b^4F_{2\frac{1}{2}}$	61624.1	312556.1		$x^4D_{0\frac{1}{2}}^0$	115790.4	258389.8
	$b^4F_{3\frac{1}{2}}$	62705.3	311474.9		$z^4G_{5\frac{1}{2}}^0$	115876.4	258303.8
	$b^4F_{4\frac{1}{2}}$	64042.6	310137.6		$y^4F_{4\frac{1}{2}}^0$	115956.7	258223.5
					$x^4D_{1\frac{1}{2}}^0$	116584.3	257595.9
					$x^4D_{2\frac{1}{2}}^0$	117602.3	256577.9
					$x^4D_{3\frac{1}{2}}^0$	118076.5	256103.7

TABLE IV. *Identified lines in Mo IV.*

Relative intensity	λ (vac.)	ν	Designation	Mult. No.	Relative intensity	λ (vac.)	ν	Designation	Mult. No.
5	2140.98	46707.6	$b^4F_{3\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	4	1805.99	55371.2	$b^4F_{3\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3
10	2114.43	47294.0	$b^4F_{4\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	2	1795.63	55690.9	$b^4F_{1\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	3
15	2092.54	47788.8	$b^4F_{2\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	3	1786.41	55978.2	$b^4F_{2\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	3
50	2061.03	48519.5	$b^4F_{1\frac{1}{2}}-z^4G_{2\frac{1}{2}}^0$	1	3	1771.40	56452.4	$b^4F_{2\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3
25	2056.29	48631.3	$b^4F_{2\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1	15	895.413	111680.3	$a^4F_{3\frac{1}{2}}-z^4G_{4\frac{1}{2}}^0$	4
20	2024.43	49396.7	$b^4F_{4\frac{1}{2}}-z^4G_{4\frac{1}{2}}^0$	1	40	894.803	111756.5	$a^4F_{1\frac{1}{2}}-y^4F_{1\frac{1}{2}}^0$	5
70	2011.57	49712.5	$b^4F_{2\frac{1}{2}}-z^4G_{3\frac{1}{2}}^0$	1		894.768	111760.8	$a^4F_{4\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	5
10	1994.72	50132.4	$b^4F_{2\frac{1}{2}}-y^4F_{1\frac{1}{2}}^0$	2	50	891.735	112141.0	$a^4F_{2\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	5
20	1991.41	50215.7	$b^4F_{3\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	2	60	886.050	112860.4	$a^4F_{3\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	5
10	1977.19	50576.8	$b^4F_{4\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2	5	885.575	112921.0	$a^4F_{1\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	5
80	1971.06	50734.0	$b^4F_{3\frac{1}{2}}-z^4G_{4\frac{1}{2}}^0$	1	10	884.816	113017.8	$a^4F_{4\frac{1}{2}}-z^4G_{5\frac{1}{2}}^0$	4
10	1966.06	50863.1	$b^4F_{1\frac{1}{2}}-y^4F_{1\frac{1}{2}}^0$	2	100	884.188	113098.1	$a^4F_{4\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	5
20	1949.44	51296.9	$b^4F_{2\frac{1}{2}}-y^4F_{2\frac{1}{2}}^0$	2	10	878.430	113839.4	$a^4F_{2\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	5
100	1929.24	51833.8	$b^4F_{4\frac{1}{2}}-z^4G_{5\frac{1}{2}}^0$	1	2	875.674	114197.7	$a^4F_{3\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	5
80	1926.26	51914.1	$b^4F_{3\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2	50	867.921	115217.9	$a^4F_{4\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	6
10	1926.26	51914.1	$b^4F_{4\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	2	20	863.629	115790.4	$a^4F_{1\frac{1}{2}}-x^4D_{0\frac{1}{2}}^0$	6
20	1886.96	52995.3	$b^4F_{2\frac{1}{2}}-y^4F_{3\frac{1}{2}}^0$	2	20	863.526	115804.3	$a^4F_{2\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	6
30	1877.88	53251.4	$b^4F_{3\frac{1}{2}}-y^4F_{4\frac{1}{2}}^0$	2	25	863.235	115843.3	$a^4F_{3\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	6
	1850.69	54033.9	$b^4F_{4\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	3	10	859.716	116317.5	$a^4F_{3\frac{1}{2}}-x^4D_{3\frac{1}{2}}^0$	6
30	1821.59	54897.0	$b^4F_{3\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	3	10	857.748	116584.3	$a^4F_{1\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	6
	1821.59	54897.0	$b^4F_{1\frac{1}{2}}-x^4D_{0\frac{1}{2}}^0$	3	5	856.001	116822.3	$a^4F_{2\frac{1}{2}}-x^4D_{2\frac{1}{2}}^0$	6
20	1819.50	54960.2	$b^4F_{2\frac{1}{2}}-x^4D_{1\frac{1}{2}}^0$	3					

TABLE V. *Term values and square roots of term values.*

Electron configuration	Terms	Yt I	Diff.	Zr II	Diff.	Cb III	Diff.	Mo IV
$4d^25p$	$^4D_{3\frac{1}{2}}^0$	29255.9		81762.5		156416.9		256103.7
		171.4	(114.5)	285.9	(109.6)	395.5	(110.6)	506.1
	$^4F_{4\frac{1}{2}}^0$	30682.3		82795.5		158217.1		258223.5
		175.1	(112.6)	287.7	(110.0)	397.7	(110.4)	508.1
	$^4G_{5\frac{1}{2}}^0$	33050.0		83866.3		158943.2		258303.8
		181.8	(107.8)	289.6	(108.9)	398.5	(109.7)	508.2
$4d^25s$	$^4F_{4\frac{1}{2}}$	51338.3		113339.0		199630.2		310137.6
		226.6	(110.1)	336.7	(110.1)	446.8	(110.1)	556.9
$4d^3$	$^4F_{4\frac{1}{2}}$	33027.8		110904.3		225065.6		371321.6
		181.7	(151.3)	333.0	(141.4)	474.4	(135.0)	609.4

diagram. Most of the lines corresponding to these transitions in Mo IV are listed in Table IV. Term values are given in Table III. The $^4FG^0$ multiplet which came out much the strongest of the triad $^4FD^0$, $^4FF^0$, $^4FG^0$ ($4d^25s-4d^25p$) in Cb III and Mo IV was comparatively weak in the transition $^4FG^0$ ($4d^3-4d^25p$); in fact, only two of the nine lines resulting from this transition were found in Mo IV. This same phenomenon has been observed in the corresponding elements of the first long period[4] and is in agreement with Kronig's principle that the intensities of multiplets resulting from combinations between a triad of high terms and a common lower term will differ, that being the strongest for which the change ΔL in the term quantum numbers is the same as the change Δl in the electron transition.

The probable error of the wave-lengths is

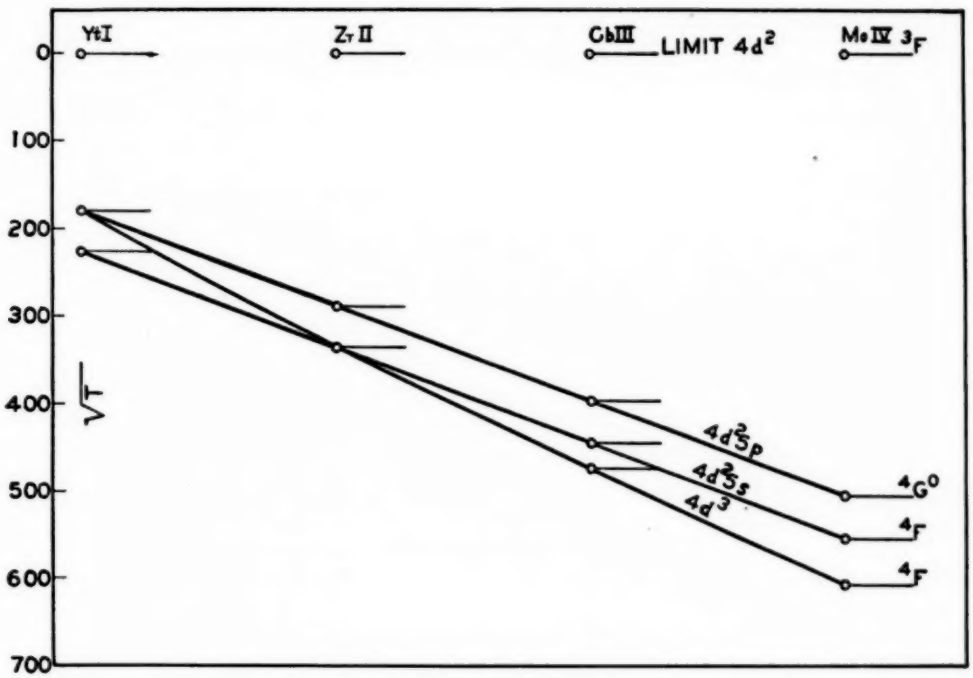

FIG. 1. Energy levels and the Moseley law.

[4] H. E. White, Phys. Rev. **33**, 672 (1929).

estimated to be less than 0.05A for columbium and molybdenum.

The Landé interval rule for term separations is fairly closely followed in both elements, especially for the lower lying terms.

The absolute term values given in Tables I and III have resulted from a linear extrapolation of the square root of the $^4F_{4\frac{1}{2}}$ ($4d^2 5s$) term of Yt I[2] and Zr II[3] which are now known more accurately than they were at the time the Cb III terms were computed by Gibbs and White.[1]

Table V gives the absolute term values and their square roots for the sequence Yt I, Zr II, Cb III and Mo IV.

Fig. 1 is a Moseley diagram of the data in Table V. It shows that for transitions involving a change in only the azimuthal quantum number, the difference in the square roots of the term values is essentially constant in going from element to element.

The author wishes to express his sincere appreciation to Professor H. E. White for his many helpful suggestions, and under whose direction this investigation has been carried on.

Kerr's Law at High Field Strengths

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Improved compensation methods similar to that of Beams have been utilized to study the validity of Kerr's law in different liquids. In the pure nonpolar carbon disulphide the law was found to hold within the limits of precision of one-eighth of one percent up to the highest field the liquid could sustain. In the polar liquids, ethyl ether and chloroform, on the other hand, easily measurable deviations were found. Curves showing the variation of the Kerr constant as a function of the electric field strength are given for ethyl ether at −78.5° C and chloroform at −22.5° C.

KERR'S law states[1] that if n_p and n_s are the refractive indices for the components of the light vibration parallel and perpendicular to the lines of force in a substance, their phase difference D after passing through an electric field E is

$$D \equiv 2\pi l(n_p - n_s)/\lambda = 2\pi B l E^2,$$

where λ is the wave-length of the light, l the length of the light path through the electric field and B is the Kerr constant. The constant B is characteristic of the substance and has been found to depend upon both its temperature and the wave-length of the light used. This law of Kerr's has been established within the limits of experimental error for many substances by several different investigators.[2] In the case of some polar liquids, however, Beams[3] found small but measurable deviations from Kerr's law at high field strengths. On the other hand with pure nonpolar carbon disulphide he was unable to observe a measurable departure from the law at the highest fields the liquid could sustain. Since the observations of Beams were of a qualitative nature the present work was undertaken with the view of finding the quantitative variation of B with field strength in the two polar liquids ethyl ether and chloroform. The liquid ether and chloroform are held at reduced temperatures which, according to a theory that will be discussed later in this paper, should enhance the magnitude of the effect. Kerr's law is also carefully investigated in the case of the nonpolar carbon disulphide.

[1] Beams, Rev. Mod. Phys. **4**, 133 (1932).

[2] Kerr, Phil. Mag. (4) **50**, 446 (1875); **13**, 153, 248 (1882). Chaumont, Ann. de Physique **5**, 64 (1916).

[3] Beams, Phys. Rev. **37**, 781 (1931).

Experimental Method

In the substances here investigated the values of B are such as to require a field E of several thousand volts per cm in order to bring D into a convenient range for study. This necessitates the measurement of rather high voltages the precision of which in turn limits the precision of the values obtained for the Kerr effect. Therefore, the methods adopted in this work were similar to that used by Beams[3] where the measured quantities were potential ratios instead of absolute values of the potential.

The principle of the method is indicated in Fig. 1 which shows the arrangement used for static fields. Light from the source B made parallel by the lens L and plane polarized by the Nicol prism N_1 enters the Kerr cell K_1, which becomes doubly refracting with the application of the electric field. The light then passes through a second Kerr cell, K_2, several times as long as K_1, and charged to a lower potential. If the double refraction produced in the second cell is exactly equal and opposite to that produced in the first, no light will pass the Nicol prism N_2, which is crossed with respect to N_1. This compensation may be attained by varying the ratio of the potentials V_1 and V_2 on K_1 and K_2 which is accomplished by means of a potential divider. If now the total potential is varied, the potential divider remaining unchanged, any deviation from Kerr's law will appear as a lack of compensation of the cells, and the potential ratio

must be changed in order that the compensation may be re-established. The light source was an incandescent lamp. S_1, S_2, and S_3 are small stops limiting the light to a narrow beam which passes through the center of the space between the plates of Kerr cells K_1 and K_2. W is a Wratten filter which limits the light to a narrow wave-length band. The Nicol prism N_1 is so adjusted that the plane of vibration of the electric vector makes an angle of 45° with the lines of force of the field in K_1, and the second Nicol N_2 is carefully crossed with respect to N_1. When the

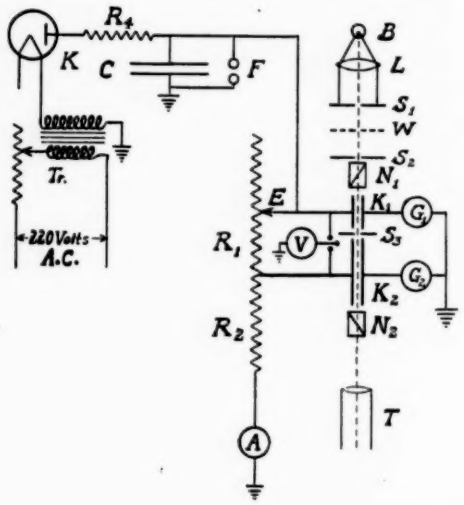

FIG. 1. Arrangement of apparatus for static fields.

liquids in the Kerr cells have constants of opposite sign the plates of K_2 are made accurately parallel to those of K_1. If the constants are of the same sign the plates of K_2 must be perpendicular to those of K_1. It is essential that the different parts of the optical system be in correct adjustment. It was observed in preliminary experiments that lack of parallelism or perpendicularity between the fields of K_1 and K_2 made it impossible to obtain complete compensation or the extinction of all the light by N_2. However, under these conditions the intensity of the light emerging from N_2 passes through a minimum as the potential ratio is varied, rather than a point of extinction. The various effects due to improper adjustment of the optical system were investigated and it was found that small errors in adjustment limit the sensitivity of the method, but otherwise have no appreciable influence upon the results.

K_1 is mounted rigidly, while K_2 is held in a specially constructed support so that it may be rotated about each of three mutually perpendicular axes. The plates of K_2 may be set approximately parallel to those of K_1 by means of a short range telescope with a cross hair. Final adjustment is made (while the potential is applied) by variation of the potential ratio and slight rotation of K_2 about the axis of the light beam until no light passes N_2. In case K_1 and K_2 contain the same liquid at the same temperature the observations are made with the aid of the telescope T. If the liquids are different, or if the two cells are at different temperatures, compensation occurs for only one wave-length for a given potential ratio due to the difference in the dispersion in the Kerr effect in the two cells. In this case it has been found satisfactory to replace T with a spectroscope and adjust for compensation for some chosen wave-length.

The electrical potential was supplied by the transformer Tr and rectified by the kenotron K, which charges the condenser C through the electrolytic resistance R_4. F is merely a safety gap. The rectified potential is applied to the adjustable electrode E of the running tap water resistances R_1 and R_2, the other end of which is grounded through the milliammeter A. G_1 and G_2 are galvanometers which measure the current flowing through the cells K_1 and K_2. V is a Wulf quartz-fiber electrostatic voltmeter used to check approximately the calibration of the potential divider and to measure the total potential across C. The ratio of the potential V_1 across K_1 to the potential V_2 across K_2 was obtained by measuring the resistance ratio

$$\frac{V_1}{V_2}=\frac{R_1 I_{G_2}+(R_1+R_2)I_A}{R_2 I_A}=\frac{R_1+R_2}{R_2}\ \text{approximately.}$$

Since the resistances of K_1 and K_2 were always very high in comparison with R_1 and R_2 where this method was used, i.e., the currents through K_1 and K_2 were always less than 2×10^{-8} amp. while that through R_1 and R_2 was greater than 10^{-3} amp. It was observed that the ratio $(R_1+R_2)/R_2$ could be obtained approximately from the position of the moving electrode E, which was suspended

in a uniform Pyrex tube filled with running tap water, showing that the fall of potential across the water resistance was linear to a first approximation.

Since the majority of substances are somewhat conducting, especially those showing marked polarity, a second method therefore was developed which utilized impulsive potentials and thus removed the difficulties inherent in the steady potential method. The potential is applied by the discharge of a spark gap, and quickly removed before field inhomogeneity in the Kerr cell had time to develop. Of the several circuits tried the one finally adopted is shown in Fig. 2.

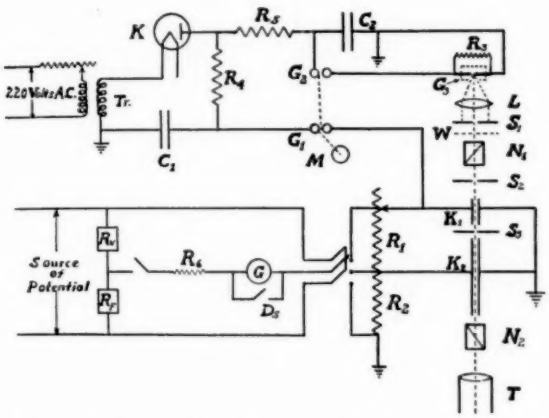

FIG. 2. Arrangement of apparatus for impulsive fields.

The optical arrangement is similar to that of Fig. 1 except that a magnesium spark gap G_3 now acts as the light source. The condensers C_1 ($2.8\times10^{-8}F$) and C_2 ($3.2\times10^{-8}F$) and the spark gaps G_1 and G_2 are charged by a 5 kw transformer (operated by a 220 volt constant potential a.c. generator) and the kenotron K through the non-inductive resistances R_4 and R_5. Ultraviolet light from the mercury arc M passes through a tube to fall in a small spot on the surface of the cathode of the gap G_1 to avoid overvolting. When the potential on this gap reaches the breakdown value a discharge occurs, and the resulting ultraviolet light irradiates G_2, which immediately discharges, as it has been set to be slightly overvolted.[4] The breakdown of G_2 then causes the discharge of the small enclosed magnesium gap G_3, which is the source of illumination. This gap was constructed from magnesium rods 5 mm in diameter enclosed in a groove between pieces of insulating asbestos board. The light was emitted through a small opening 5 mm square. In this way the very intense discharge was confined to a narrow path. The electrolytic resistance R_3 prevents the floating of the part of the circuit connecting G_2 and G_3. Heating of the electrodes was prevented in G_1 and G_2 by small jets of compressed air directed on the gaps.

The discharge of G_1 impresses a potential surge upon the electrolytic ($CuSO_4$ in water) resistances R_1 and R_2, which have a value of the order of 2×10^3 ohms. When G_2 is properly adjusted the discharge of G_3 is practically simultaneous with that of G_1, and the intensity of the illumination from G_3 is approximately a maximum at the same instant in which the potential on the cells is a maximum.

The potential applied to K_1 is derived from the width of G_1, as it is not necessary to know this with very high precision. The ratio of the potential across K_1 to that across K_2 was measured by a separate experiment in which the circuits at the lower left (Fig. 2) were connected as indicated forming a Wheatstone bridge. After a balance it is evident that the ratio of the potential across K_1 to that across K_2 is equal to $(R_V+R_F)/R_F$. This of course is true only when the capacity of K_1 and K_2 are very small in comparison with C_1 and Ohm's law holds for impulsive discharges. Evidence for the correctness of this latter assumption is supplied by the straight line obtained for CS_2 (Fig. 4). Both alternating and direct-current bridge methods were used and found to give the same results within the limits of precision. R_F is a fixed resistance of 10^4 or 2×10^4 ohms. R_V is a decade plug type resistance box with a range of 2×10^4 ohms, adjustable in one ohm steps. The potential was applied from a battery of 180 volts.

As already mentioned complete compensation of the elliptically polarized light produced in K_1 by that produced in K_2 can be obtained only for one wave-length of light (in practice a narrow band) when the liquids in K_1 and K_2 are dissimilar. In the experiments employing the magnesium spark as a light source the potential ratio across the two Kerr cells was adjusted to give compensation for the bright line at 4481A. The

[4] Street and Beams, Phys. Rev. **38**, 416 (1931).

light was viewed through a spectroscope and filters to cut out the strong Mg lines other than 4481.

With both of the above experimental methods, the validity of Kerr's law was established for pure, freshly distilled carbon disulphide, which is nonpolar. Since the Kerr constant of this liquid does not change with the potential, a cell containing carbon disulphide was thereafter used as a standard to compensate a second cell containing either ethyl ether or chloroform, both of which are polar. The cell K_2 containing carbon disulphide was maintained at room temperature or a few degrees above. The polar liquids were tested at room temperature and at reduced temperatures. In particular ethyl ether was tested at a temperature of -78.5°C, by using "dry ice" as the refrigerant.

The Kerr cells were constructed of Pyrex tubing 3.8 cm in diameter. The plates were of nickel, rigidly supported by large tungsten wires sealed in the sides of the cells. A special feature of the construction is shown in Fig. 3b. The small tubes mounted on the plates limit the light to a narrow beam which passes through the center of the field, well out from the surface of the electrodes, and no light stops are necessary. The method of thermal insulation of the low temperature cell is shown in Fig. 3a, and the details of the construction of the cell in Fig. 3c.

In the experiments in which a polar liquid in one cell at reduced temperature was balanced against carbon disulphide in a second cell as standard, any appreciable error due to change in temperature of the latter was prevented by maintaining the carbon disulphide cell in a thermally insulated box held at a constant temperature of 27.6°C by heating coils operated by a mercury thermostat. It was observed that the change of temperature of the carbon disulphide was less than 0.01°C throughout a series of observations.

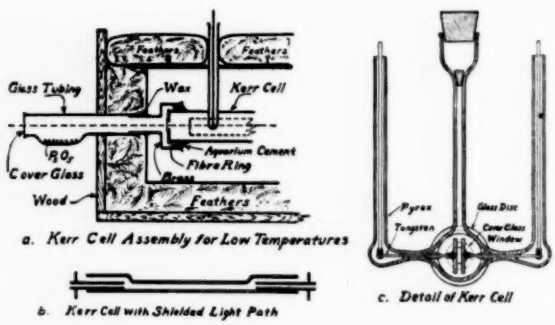

FIG. 3. (a) Method of thermal insulation of low temperature cell. (b) Kerr cell with shielded light path. (c) Detail of low temperature cell.

The Nicol prisms were of the Glan-Thompson type, with end surfaces 7 mm square. The spectroscope was of the direct vision type and had sufficient resolving power to permit the setting of the compensation band with an accuracy of 3A in the spectral range employed. Preliminary experiments with impulsive fields led to the adoption of copper sulphate as the most satisfactory electrolyte for the resistances R_1 and R_2 which were made of two sections of uniform Pyrex tubing 1.8 cm in diameter, joined by a short section of copper tubing of equal internal diameter which formed the upper of the two stationary electrodes. The lower electrode was also of copper. The moving electrode was made of a copper rod 8 mm in diameter and 80 cm long. It is very important to have the copper in each of the above cases as pure as possible. To minimize any possible variations in resistance due to convection currents in the liquid, the level of the electrolyte was kept only a few cm above the lower end of the moving electrode when adjusted for compensation. This insured that whatever change in temperature was produced by the high potential discharge would be uniform throughout the column of liquid, and thus the resistance ratio for any given setting of the moving electrode would remain constant with time. The resistance was surrounded by running tap water. As a further precaution the bridge measurement was always made immediately after the high potential discharge occurred, the measurement in all cases being completed within thirty seconds.

Bakers Analyzed Chemicals of C.P. quality were used. In all cases the cells were thoroughly washed with the pure, freshly distilled liquid before filling. The carbon disulphide was always taken from a freshly opened bottle; placed immediately in a still, and distilled at atmospheric pressure directly into the cell, the high and low boiling fractions being discharged. The ethyl ether used was C.P. anhydrous, distilled over sodium by the manufacturer, and supplied in

lead sealed 1 lb. cans. It was found possible to reduce materially the conductivity by redistillation directly into the Kerr cell. Special precautions were necessary to remove moisture, which if present would form into solid particles while the temperature was lowered. These crystals gradually combine to form large flakes as the temperature of "dry ice" is reached, and finally settle to the bottom of the cell, well out of the field of view. To remove moisture or other impurities in the ether the sealed cans were packed for a number of hours in dry ice. They were then removed, the seal broken, and the ether passed through a specially constructed filter maintained at a temperature well below 0°C directly into the distilling apparatus, which had previously been dried by drawing clean dry air passed over $CaCl_2$ and P_2O_5 through it for many hours.

After being carefully dried with clean air passed over $CaCl_2$ and P_2O_5 the Kerr cell designed to receive the ether was packed in dry ice as shown in Fig. 3a. The ether was then slowly distilled directly into the cold cell (great care being taken that no moist air came in contact with the ether at any stage of the process). C.P. chloroform was prepared for use in the manner similar to that just described. Since chloroform freezes at −70°C it was necessary to replace the dry ice with a mixture of ice and salt.

As mentioned previously Kerr's law was found to be valid for pure carbon disulphide by both the methods just described. Fig. 4 shows the ratios of the square of the electric field strength in K_1 to that in K_2, or E_1^2/E_2^2, plotted as a function of the field strength E_1 in K_1 for carbon disulphide. It will be observed that the curve is a horizontal line which shows that the Kerr constant B_1 (Eq. 1) is independent of E within the possible experimental error of one-eighth of one percent. In the case of ethyl ether, however, a lowering of the Kerr constant B was found at high field strengths. Fig. 5 shows a similar graph of E_1^2/E_2^2 plotted as a function of E_1 when K_1 was filled with ethyl ether at −78.5°C and K_2 with carbon disulphide at 26.5°C. It will be noted that the curve bends upward at the higher field strengths. Since the Kerr constant of carbon disulphide is not a function of the field strength

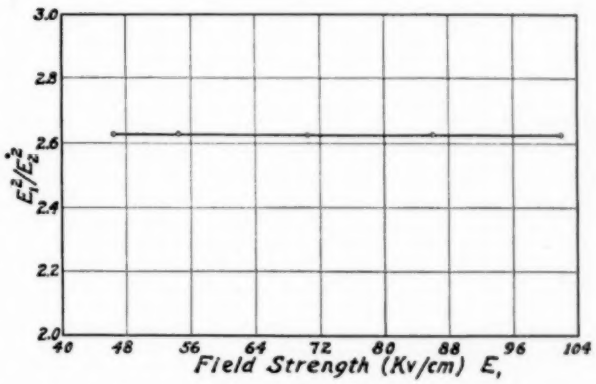

FIG. 4. Validity of Kerr's law for carbon disulphide. Precision one-eighth of one percent.

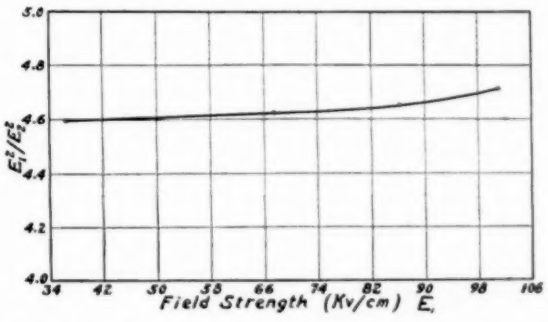

FIG. 5. Deviation from Kerr's law at high field strengths for ethyl ether at −78.5°C. Precision one-eighth of one percent.

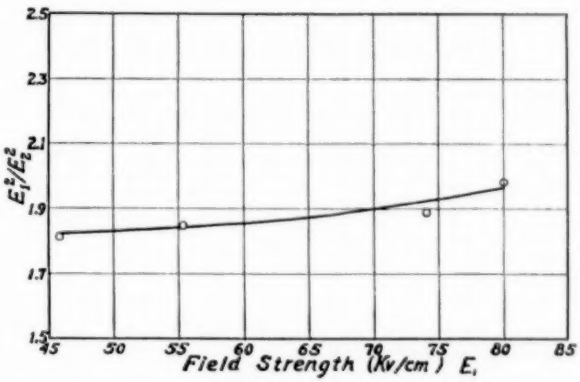

FIG. 6. Deviation from Kerr's law at high field strengths for chloroform at −22.7°C. Precision three-fourths of one percent.

and remains constant, Fig. 5 gives the variation of the Kerr constant B_1 of ether as a function of the field E_1, i.e., $B_1/B_2 \propto E_2^2/E_1^2$. Fig. 6 shows a graph of E_1^2/E_2^2 plotted as a function of E_1 when K_1 contains chloroform at −22.7°C. The observations were not so precise as those in Fig.

5, yet they show unmistakable evidence of the existence of a deviation from Kerr's law at high field strengths.

Most of the troublesome sources of error that creep into the measurement of the Kerr effect by steady field methods are practically eliminated by the use of the second or impulsive field method described above without sacrificing precision. It can easily be seen that the precision of the arrangement described in this paper is proportional to the intensity of the light source and to the length of time that the electric field is applied. In the case of the impulsive field method the potential is applied for from 10^{-4} to 10^{-5} of the time only, so that the sensitivity is cut down by the above factor. In order to compensate for this it was necessary to increase the intensity of the light source while the field was on. This was accomplished by so timing the source spark G_3 that it was at maximum brilliancy while the field was applied. Hence, since the maximum intensity of the spark is perhaps as much as a thousand times that of the small incandescent lamp used, and since in addition the spark gives off the brilliant 4481 Mg line, the precision lost by the short time of application of the field is nearly compensated by the increased light intensity. Another source of error that the impulsive field method practically eliminates even in quite conducting liquids is the heating effect due to the conduction current. Computations show that in the above experiments the heating of the liquid by this conduction current was too small to affect the results. Another heating effect that may become appreciable if the field is applied and removed quickly enough is due to the orientation of the molecules themselves, i.e., the electric absorption.[5] However, this effect is negligible because the time of application and removal of the field was long in comparison with the time required for the molecules of the substance to be oriented and deoriented. For this same reason the possible lag in the Kerr effect is far too small to introduce appreciable error.[6] The time required for electrostriction to take place completely in the liquid is of the same order of magnitude as the times used in the experiment, but any error introduced would be inappreciable. This was checked by varying the time of application and removal of the potential. Perhaps the most serious error in measurements of the Kerr effect in liquids that are even slightly conducting is the field distortion resulting from a sort of space charge or concentration of ions and impurities in certain regions in the liquid. In the above experiments no variation of the ellipticity of the light across the field of view from the surface of one plate to the other could be detected when the light stops were removed, which showed that this source of error was almost negligible. This is also in accord with an approximate calculation. An added precaution was taken to keep the light beam confined to the region in the center of the field when observations were being made. Other possible sources of error such as variations in the distance between the plates, etc., were too small to be appreciable, as is shown by the straight line Fig. 4, found in the case of carbon disulphide.

An attempt was made to observe the variation of B in mixtures of carbon disulphide and chloroform. Since the Kerr constants of these two liquids are respectively positive and negative it is possible to obtain a mixture of the two which will give zero Kerr effect for a given wave-length of light. The composition of this mixture cannot be computed directly from the Kerr constants of the constituents, but must be found by a method of trial and error. Thus at 26°C a mixture of 37.8 percent carbon disulphide and 62.2 percent chloroform gives zero Kerr effect for the green line of mercury with a compensation band similar to that described above for dissimilar liquids in separate cells. Variation of the potential applied to the cell containing the mixture did not produce a shift of the band of sufficient magnitude to be measurable with the rather low precision (one or two percent) attained.

Discussion of Results

The variation of the Kerr constant with increase in field is what may be expected from theory in the case of polar liquids. On the Langevin-Born theory[7, 1] the Kerr constant B

[5] Debye, *Polar Molecules*, Chem. Cat. Co., Chapter 5, (1928).

[6] Beams, Rev. Sci. Inst. **1**, 780 (1930).

[7] See Debye, Handbuch der Radiology **6**, 754–776 (1925), Leipzig.

can be written

$$B \propto [(n_0^2-1)(n_0^2+2)(\epsilon+2)^2/n_0 T][1+\phi(\mu^2/T)]$$

where n_0 is the index of refraction ϵ is the dielectric constant, T the absolute temperature and μ the electric moment. Numerous experimenters[8] have shown that a decrease in the dielectric constant occurs as the field is increased, and Debye has proposed a theory showing that such a variation should be expected. Unfortunately measurements of the variation of ϵ with field strength are not available, in the substances at the temperature used, so it is possible to make only a very rough estimate of the variation to be expected in B with field strength. Such an estimate shows that the order of magnitude of the variation of B with E in ether and chloroform is about what might be expected. The theory, however, is necessarily very uncertain, as it is based on the Clausius-Mossotti hypothesis, from which there may be very marked deviations especially in polar liquids.

In conclusion the author wishes to acknowledge his indebtedness to Professor J. W. Beams, under whose direction and guidance the experiments were carried out, and to each of the other members of the staff of this laboratory who were consulted freely during the progress of the work.

[8] Debye, *Polar Molecules*, Chem. Cat. Co. (1928).

The Diamagnetism of Carbon Tetrachloride, Benzene and Toluene at Different Temperatures

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An account is given of experiments on the variation, with temperature, of the diamagnetism of benzene, toluene and carbon tetrachloride. The results indicate that the mass susceptibilities of these liquids decrease only slightly, if at all, with increasing temperatures; the change was less than one percent in each case.

IN a previous paper,[1] a description was given of a new and very sensitive device for measuring very small changes in magnetic susceptibility of liquids. Some preliminary results on the variation with temperature of the diamagnetism of water were also given. The results obtained showed certain anomalies, which might possibly be explained on the assumption that the diamagnetism of water depends somewhat on its recent thermal history. If, with the same apparatus, such anomalies are not shown in normal liquids, they cannot be due to peculiarities of the apparatus itself and their interpretation must be looked for elsewhere.

It was therefore decided to make a series of experiments on certain liquids which, in view of their other known properties, might be expected to be normal in their magnetic behavior. The liquids selected were carbon tetrachloride, benzene and toluene.

THEORY AND PROCEDURE

The apparatus used in the present investigation was the same as that used in the investigation mentioned above; for details relating to it the reader is referred to the previous paper.[1]

The principle of the measuring device employed, called a manometric balance, is that of balancing the actions of two magnetic fields on two liquid columns (joined by a mercury column and contained in Pyrex tubes). The strengths of the magnetic fields at the free surfaces, or menisci, being designated by H and H_0, the condition for balance is:

$$\tfrac{1}{2}\kappa H_0^2 = \tfrac{1}{2}\kappa_0 H^2, \qquad (1)$$

where κ indicates the volume susceptibility of the liquid whose meniscus is in the field H_0, and κ_0 that of the liquid whose meniscus is in the field H. It is customary to express the results of susceptibility measurements in terms of specific susceptibilities, and in our case these are designated by χ, χ_0 so that: $\chi = \kappa/\rho$, and $\chi_0 = \kappa_0/\rho_0$, where ρ, ρ_0 denote the densities of the liquids. We can then write in place of Eq. (1):

$$\chi/\chi_0 = (\rho_0/\rho)(H/H_0)^2. \qquad (2)$$

In general χ_0 represents the specific susceptibility of a standard liquid such as water maintained at a standard temperature T_0, and χ the specific susceptibility of the liquid under test at some temperature T. The densities ρ, ρ_0 can usually be derived from the tables, and if not, can be specifically determined.

Balance is actually effected as follows: The meniscus of one of the liquids (that under experimentation) being kept in a constant field H_0, the other is moved until it reaches a position where the corresponding field strength H is such as to produce a balance, and the positions of the menisci with respect to their corresponding fields are then determined with the aid of two micrometer-telescopes.

The ratio of the magnetic field strengths H, H_0 is determined by a process of calibration whereby a solution of nickel chloride, whose volume susceptibility κ_n can be determined as explained

[1] A. P. Wills and G. F. Boeker, Phys. Rev. **42**, 687 (1932).

below, is placed in one branch of the apparatus with its meniscus in the constant field H_0. This solution is balanced against pure water in the other branch of the apparatus, the meniscus of which, at balance, is in a field H, both liquids being maintained at the standard temperature. Usually the surfaces of the liquids were in contact with helium gas, the susceptibility of which is negligible; but in the process of calibration it is more convenient to have the menisci in contact with air; the susceptibility of the air must then be taken into account.

If κ_a denote the volume susceptibility of the air, when balance obtains we shall then have in place of (1):

$$\tfrac{1}{2}(\kappa_n-\kappa_a)H_0^2=\tfrac{1}{2}(\kappa_0-\kappa_a)H^2$$

and hence:

$$\left(\frac{H}{H_0}\right)^2=\frac{\kappa_n/\kappa_0-\kappa_a/\kappa_0}{1-\kappa_a/\kappa_0},$$

where κ_a/κ_0 is a small quantity. With sufficient approximation the last equation can be written:

$$\left(\frac{H}{H_0}\right)^2=\frac{\kappa_n}{\kappa_0}+\frac{\kappa_a}{\kappa_0}\left(\frac{\kappa_n}{\kappa_0}-1\right)+\left(\frac{\kappa_a}{\kappa_0}\right)^2\left(\frac{\kappa_n}{\kappa_0}-1\right). \quad (3)$$

To determine the value of κ_n in terms of κ_0, a solution of nickel chloride in water was prepared which was neutral against helium gas at the standard temperature 22.7°C. With this neutral solution, several diamagnetic solutions were made, each of which was prepared by adding a mass m of neutral solution to a mass μ of pure water. By Wiedemann's law:

$$(m+\mu)\chi_n=\mu\chi_0,$$

whence

$$\chi_n/\chi_0=1/(1+\delta), \quad \text{where} \quad \delta=m/\mu.$$

If ρ_n, ρ_0, respectively, denote the density of such a diamagnetic solution and that of pure water, and if χ_n, κ_n denote the mass and volume susceptibilities of the diamagnetic solution, and χ_0, κ_0 those of pure water, then, since $\rho_n\chi_n=\kappa_n$ and $\rho_0\chi_0=\kappa_0$, we can write:

$$\kappa_n/\kappa_0=(\rho_n/\rho_0)(1/(1+\delta)). \quad (4)$$

The Magnetic Susceptibilities of Carbon Tetrachloride, Benzene and Toluene Relative to Water

In order to determine the ratio of the magnetic susceptibility of each organic liquid used to that of water, the liquid was balanced against an aqueous nickel chloride solution, the susceptibility of which was known in terms of that of water. The menisci being in contact with air, when balance obtains we have in place of (1):

$$\tfrac{1}{2}(\kappa_L-\kappa_a)H^2=\tfrac{1}{2}(\kappa_n-\kappa_a)H_0^2 \quad (5)$$

where κ_L is the volume susceptibility of the organic liquid; in what follows the subscript L refers to this liquid. The other symbols have the significance previously assigned to them. From Eqs. (4) and (5) we obtain:

$$\frac{\chi_L}{\chi_0}=\frac{\rho_n}{\rho_L(1+\delta)}\left[\left(\frac{H_0}{H}\right)^2+\frac{\kappa_a}{\kappa_n}\left(1-\left[\frac{H_0}{H}\right]^2\right)\right]. \quad (6)$$

The mass susceptibility of water at 22.7°C is taken as -0.720×10^{-6},[2] and, with this value for water, the value for the mass susceptibilities of carbon tetrachloride, benzene and toluene, given in the last column of Table I, were obtained.

The benzene and carbon tetrachloride were of the best available grade obtainable from

[2] -0.720×10^{-6} is the commonly accepted value for 20°C.

Table I. *Mass susceptibilities.* I.C.T., International Critical Tables (Pascal, Ishiwara); T and S, Trew and Spencer, Proc. Roy. Soc. **A131**, 209 (1931); S.P.R., S. P. Ranganadham, Ind. J. Phys. **6**, Part 5, 421 (1931); R and S, S. R. Rao and G. Sivaramakrishnan, Ind. J. Phys. **6**, Part 6, 509 (1932); G.F.B., Gilbert F. Boeker.

	I. C. T.	T and S	S. P. R.	R and S	G. F. B.
Carbon tetrachloride	-0.429×10^{-6}	-0.542×10^{-6}	-0.4313×10^{-6}	-0.432×10^{-6}	-0.433×10^{-6}
Benzene	$-.712\times10^{-6}$	$-.732\times10^{-6}$	$-.7042\times10^{-6}$	$-.702\times10^{-6}$	$-.698\times10^{-6}$
Toluene	$-.729\times10^{-6}$	——	——	——	$-.712\times10^{-6}$

Merck; the toluene was a C.P. product of Eimer and Amend and was redistilled. Each liquid was vigorously boiled before using in order to eliminate dissolved gases.

Variations of Susceptibilities with Temperatures

(a) Carbon tetrachloride

In Fig. 1 a curve is shown giving the ratio of the mass susceptibility at temperature T to

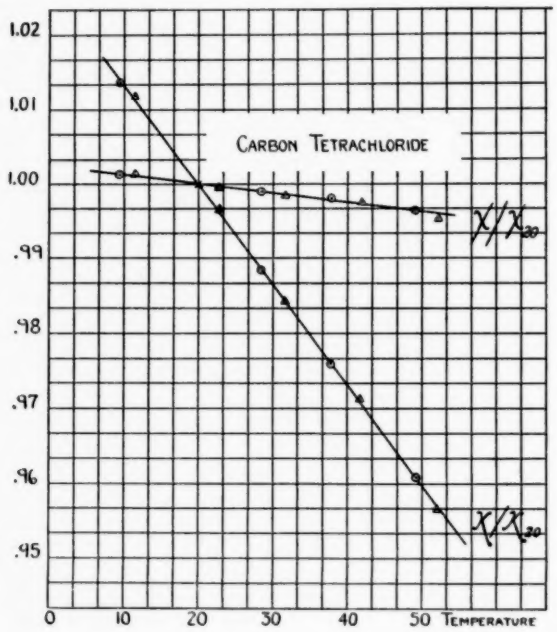

Fig. 1. The ratios of the susceptibilities of carbon tetrachloride *vs.* temperature.

that at 20°C for the temperature range 10 to 50°C and also a curve is given for the volume susceptibility of a sample of carbon tetrachloride obtained from the Merck Chemical Company; the points represented by the Δ's indicate results of an experiment on a sample of carbon tetrachloride obtained from the Baker Chemical Company.

The data from which the curves for Merck's carbon tetrachloride were constricted are given in Table II. The temperatures T in the first column indicate temperatures at which the liquid was balanced against the same liquid kept at the standard temperature (22.7°C). The

Table II. *Data on carbon tetrachloride.*

T	$(H/H_0)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_t	χ/χ_{20}
9.5	1.0173	1.0139	0.9874	1.0011
22.7	1.0000	0.9966	1.0033	0.9999
28.5	0.9919	0.9885	1.0105	0.9989
37.95	0.9793	0.9760	1.0223	0.9978
49.4	0.9642	0.9609	1.0372	0.9966

ratios[3] of the field strengths $(H/H_0)^2$ at the menisci when balance obtains, are given in the second column. From Eq. (1) these numbers represent the ratios of the volume susceptibilities of the liquid at temperatures T to that at the standard temperature (22.7°C). The ratios of the volume susceptibilities to that at 20°C, given in the third column, were obtained from numbers in the second column by a simple transformation; to determine the corresponding ratios of the mass susceptibilities, given in the last column, the ratios of the volume susceptibilities in the third column were multiplied by the ratios of the densities given in the fourth column. The density ratios were obtained from data given in the *International Critical Tables.*

No variation of the magnetic susceptibility of carbon tetrachloride depending on its previous thermal treatment could be detected; the susceptibility of the liquid was measured at 22.7°C, then the temperature was lowered to about 4°C and held there for approximately one-half hour; the temperature was again raised to 22.7°C and after a period of twenty minutes, the magnetic susceptibility was found to be the same within experimental error. Corresponding results were found for similar experiments at higher temperatures.

(b) Benzene

In Fig. 2 curves are given for χ/χ_{20} and for κ/κ_{20} as functions of the temperature for benzene obtained from Merck Chemical Company, obtained in a manner quite analogous to that outlined for carbon tetrachloride. The results shown by these curves were confirmed by repeated experiments on the same liquid. The results of a temperature run upon a sample of benzene obtained from the Baker Chemical

[3] The method of obtaining this ratio is described, in detail, in the previous paper, reference 1.

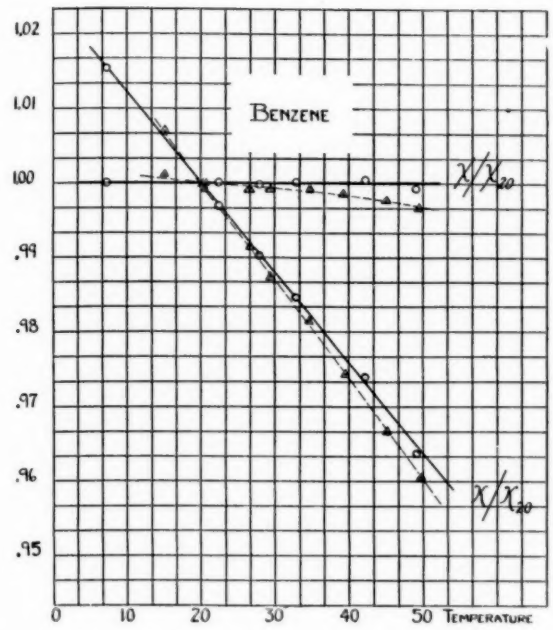

FIG. 2. The ratios of the susceptibilities of benzene *vs.* temperature.

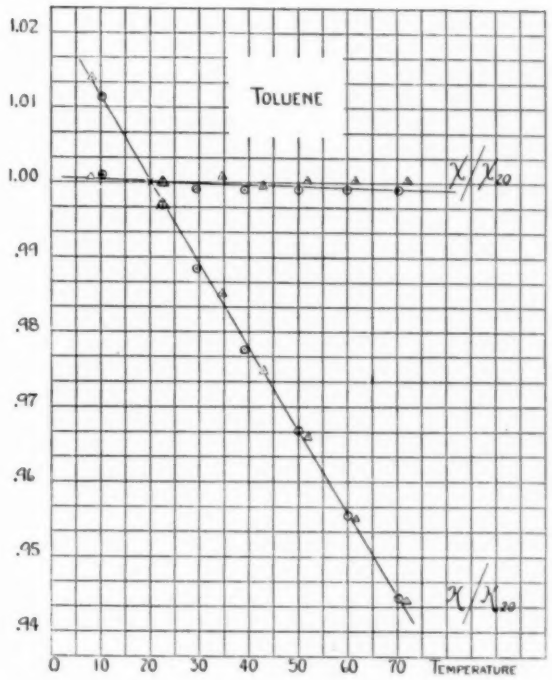

FIG. 3. The ratios of the susceptibilities of toluene *vs.* temperature.

Company are indicated by the Δ's. The lack of agreement is striking, and is probably due to a difference in the composition of the liquids themselves.

The data for the curves shown above for Merck's benzene are given in Table III. The

TABLE III. *Data for benzene.*

T	$(H/H_c)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_T	χ/χ_{20}
7.75	1.0184	1.0153	0.9850	1.0000
22.7	1.0000	0.9970	1.0033	1.0003
27.9	0.9931	0.9901	1.0098	0.9998
32.8	0.9875	0.9845	1.0159	1.0002
42.15	0.9765	0.9736	1.0279	1.0007
49.3	0.9666	0.9637	1.0371	0.9995

significance of the numbers in the various columns and the method of finding them are identical with those outlined above in the case of carbon tetrachloride. As in the case of carbon tetrachloride, no variation of the magnetic susceptibility with previous thermal treatment could be detected.

(c) Toluene

In Fig. 3 curves are given for χ/χ_{20} and for κ/κ_{20} as functions of the temperature, for toluene obtained from the Baker Chemical Company. The results of a temperature run on a sample of toluene obtained from Eimer and Amend are indicated by Δ's; this sample was carefully redistilled before using.

The data for the run on Baker's toluene are given in Table IV; as in the case of carbon

TABLE IV. *Data on toluene.*

T	$(H/H_0)^2=\kappa/\kappa_{22.7}$	κ/κ_{20}	ρ_{20}/ρ_T	χ/χ_{20}
10.25	1.0142	1.0111	0.9897	1.0007
22.7	1.0000	0.9969	1.0029	0.9998
29.95	0.9917	0.9886	1.0108	0.9993
39.9	0.9806	0.9776	1.0220	0.9991
50.0	0.9699	0.9669	1.0336	0.9994
60.0	0.9586	1.9556	1.0456	0.9992
70.1	0.9473	0.9444	1.0581	0.9993

tetrachloride and benzene, no variation of the magnetic susceptibility with previous thermal treatment could be found.

DISCUSSION

The variation of the magnetic susceptibilities of diamagnetic liquids has been studied by

various observers. S. R. Rao and G. Sivaramakrishnan[4] conclude on the basis of the as yet unpublished work of N. Iyer that the mass susceptibility of the "ordinary" (normal ?) organic liquids do not vary with temperature. On the other hand they conclude, on the basis of the experiments of R. N. Mathur,[5] that if the liquids are highly associated this variation may become quite large. Mathur himself concludes, on the basis of his experiments, that the variation of the mass susceptibilities with temperature of the aromatic liquids is greater than for the aliphatic liquids. The results, however, of the present investigation on the aromatic liquids benzene and toluene indicate that the variation of their mass susceptibilities with temperature is very small, being less than one-half of a percent.

In the experiments described above, under favorable conditions[6] a variation in the ratio of volume susceptibilities of ± 0.0002 can be detected; it is estimated that as far as the measurements themselves are concerned (neglecting impurities and assuming the validity of Wiedemann's law), the results may be in error by about ± 0.0009.

Cognizance was of course taken of possible errors due to the presence of the vapor of the liquid in contact with the menisci; but various tests showed that the mass of this vapor was far from that of a saturated vapor at the temperature of the warmer meniscus and hence that no correction on account of the vapor was necessary.

The results obtained with the normal liquids, benzene, toluene and carbon tetrachloride constitute a thorough test of the behavior of the apparatus, and make it improbable that the apparent anomalies described in the previous paper on water[1] can be attributed to the apparatus itself.

I wish to express my appreciation for the help given to me by Professor A. P. Wills, under whose direction this investigation was carried out. I also wish to thank Mr. D. B. Woodbridge for many valuable suggestions and continued assistance.

[4] Ind. J. Phys. **6**, Part 6, 527 (1932).

[5] Ind. J. Phys. **6**, Part 3, 207 (1931).

[6] At the higher temperatures, the determination of the balance point becomes extremely difficult because of the increased drifting of the particles suspended in the liquid under test.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Spin of the Sodium Nucleus

The $^1\Pi \leftarrow {}^1\Sigma$ absorption bands of molecular sodium have been studied by Frederickson and Watson[1] and by Loomis and Wood,[2] and Urey[3] has pointed out that a distinct alteration of intensities occurs in these bands. We have measured the relative intensities of the Q-branch lines $J''=48$ to $J''=73$ of the (0, 2) band and have found that the ratio of intensities of the odd to the even lines is 1.74.

A one meter long iron tube was used as an absorption cell, which was heated by resistance coils wound around it. The sodium vapor was confined to a 40 cm central portion where the temperature was uniform within two degrees by means of streams of nitrogen gas flowing in near the windows and out through more centrally located tubes. A 500 C.P. Point-O-Lite lamp served as a continuous source.

Sets of calibration marks were placed on each photographic plate below the absorption spectrum, and relative intensities were calculated from microphotometer curves. In view of the presence of considerable background irregularities in the absorption spectrum it was found necessary to refer all lines to an average background.

The intensity of the transmitted light is given by $I=I_0e^{-\alpha}$, where I has been taken as the intensity at the middle of the line and I_0 as the intensity of the background. α is proportional to the absorption coefficient since the intensities of all the lines are measured in the same column of vapor. For the values of α encountered in this work (0.02–0.08) we may take α as a measure of the relative intensities of the lines,[4] without introducing errors greater than one or two percent.

The α's of the Q-branch lines are theoretically given by the formula:

$$\alpha = Cg(2J+1)\exp\left(-BhcJ(J+1)/kT\right)$$

where C is a proportionality factor, and $g=(i+1)(2i+1)$ for the odd lines and $i(2i+1)$ for the even lines and the other symbols have their usual meaning. If the quantity $\ln(2J+1)/\alpha - BhcJ(J+1)/kT$ is calculated for all lines and averaged for the strong and weak ones separately, the difference between the two averages gives $\ln(i+1)/i$.

Since an important source of error in such measurements may be incomplete resolution of the lines, the effect of pressure, broadening in the observed value of $(i+1)/i$ was investigated. No systematic trend of $(i+1)/i$ was observed as the nitrogen pressure was varied from 2.5 mm to 185 mm of mercury. Also, the effect on the relative values of the α's of changes in shape of the absorption lines due to the optical system has been found to be negligible.

Table I gives the observed ratios under different experimental conditions.

TABLE I.

Plate	Temp. °C	Nitrogen pressure	$(i+1)/i$
B	347	2.5 mm	1.68
C	348	27.4	1.69
D	346	103	1.81
F	347	185	1.69
G	348	185	1.85
			Aver. 1.74

The probable error in $(i+1)/i$ calculated from the deviations of the individual lines from the mean is about 0.10 for each plate.

From the observed value of 1.74 for the ratio of $i+1$ to i, we conclude that the spin of the sodium nucleus is $\frac{3}{2}$. Rabi[5] using another method has secured this same value.

J. JOFFE
HAROLD C. UREY

Department of Chemistry,
Columbia University,
New York, N. Y.,
March 24, 1933.

[1] W. R. Frederickson and W. W. Watson, Phys. Rev. **30**, 429 (1927).

[2] F. W. Loomis and R. W. Wood, Phys. Rev. **32**, 223 (1928).

[3] H. C. Urey, Phys. Rev. **38**, 1074 (1931).

[4] See formulae given by Ladenburg and Levy, Zeits. f. Physik **65**, 189 (1930).

[5] I. I. Rabi, to appear in this journal.

Purity of Zinc for Which Thermal Diffusivity Recently Was Reported

In connection with my recent paper *A Precise Determination of the Thermal Diffusivity of Zinc* which appeared in your issue of January 15, 1933, I have received a communication from the Platt Bros. & Company in which they transmit an average analysis obtained from the producers of the zinc rod, The Bunker Hill and Sullivan Mining Company, corresponding to the time the zinc was obtained from them. Since the question of chemical analysis is of considerable importance in connection with the utilization or verification of the data which I published, I give this average analysis below, together with additional data obtained from Arthur D. Little, Inc. pertaining to the specimen which I used:

Average Analysis, Bunker Hill Brand Zinc

Cadmium	0.001 to 0.002 percent
Iron	0.003 to 0.002
Lead	0.002 to 0.003
Copper	0.001

In reference 3 of my paper I should have included a supplementary statement which Arthur D. Little, Inc. made relative to their analysis: "The impurities which we determined are the ones which are normally present in commercial zinc in appreciable amounts. It may also contain traces of copper, carbon, silicon, arsenic, antimony, sulphur, tin, silver, thallium, indium and gallium." Since the receipt of the average analysis I have had Arthur D. Little, Inc. analyze a remaining portion of the specimen, about 25 grams, for copper. The report of this shows 0.001 percent of copper. Additional information relating to the determinations of cadmium and lead is stated by Arthur D. Little, Inc. as follows:

> "In the case of the cadmium determination in the zinc rod which you submitted in February, 1932, we would consider a weighable amount 0.0006 percent or more. In the case of the lead it was not practical to use such a large sample so that the degree of precision is not as great as with the cadmium. We would consider a weighable amount of the lead 0.002 percent or more.
>
> "In the case of the cadmium we obtain an increase in weight of one-tenth of a milligram with a 31 gram sample. If this were actually calculated out it would amount to 0.0003 percent. This weight is less than the degree of precision of the average commercial analytical balance so that there was considerable question as to whether there was really any cadmium present.
>
> "In the case of the lead we obtained no increase in weight whatever. We would therefore say that the cadmium was less than 0.0006 percent and the lead less than 0.002 percent."

R. H. FRAZIER
Massachusetts Institute of Technology,
March 31, 1933.

The Hyperfine Structure and Nuclear Moment of Cobalt

A number of the strong lines in the spectrum of Co I were excited in a Schüler tube cooled in liquid air and examined for hyperfine structure. Aluminum coated Fabry Perot etalons (since most of the important lines were in the region 3400 to 3900A) placed in the parallel beam of a two prism quartz spectrograph were used. Many of these lines showed rather a narrow overall hyperfine separation and with 5 to 10 mm invar separators were *partially* resolved into from two to six components. Before resolution was complete the orders began to overlap due in part to the large number of components which were present and also to the rather low resolving power of the etalons in this region. The fact that the dispersion of the spectrograph was not great enough to widely separate the many strong lines occurring in this part of the spectrum presented another serious difficulty.

Since these results indicated rather a high value for i, the nuclear moment of Co, those lines which arise from levels of high J value were examined. λλ 3465.8 and 3909.9 which have the same lower state $3d^74s^2\ {}^4F_{4\frac{1}{2}}$ originate through transitions from the levels $3d^74s4p$, ${}^4G_{5\frac{1}{2}}$ and ${}^6G_{5\frac{1}{2}}$ respectively, and possess some of the widest h.f.s. separations. Both degrade toward the red which is in keeping with the upper level (the one containing a single $4s$ electron) possessing a wide h.f.s. separation relative to the lower level. The J values of the upper levels are both $5\frac{1}{2}$ so that $2i+1$ components would result (if $i<J$). Both lines partially resolved appear to have more than 6 components, so that i for Co is at least 5/2 and very probably greater. Co possesses but one principal isotope of mass 59 so that one would expect i to be half integral; assuming this and applying the interval rule to microphotometer traces of λ 3909.9 a value of $i=7/2$ gave the best agreement between the theoretical curve and that observed, however the value $i=9/2$ is not precluded. λ 3453.5, $3d^84s\ {}^4F_{4\frac{1}{2}}-3d^84p$, ${}^4G_{5\frac{1}{2}}$ showed an h.f.s. of comparable overall separation, degrading toward the violet in keeping with the lower level having the widest separations; five components were resolved while the tail, which degraded rapidly in intensity, was broad enough to contain several components.

The results obtained therefore indicate that $5/2<i\leq 9/2$. Widest h.f.s. separations, as is usual, were observed in those levels containing a single tightly bound s electron.

It might be worth mentioning that our results both as to the method of evaporation of aluminum and the durability of such surfaces agree completely with those of Strong, Phys. Rev. **43**, 498 (1933). The surfaces of aluminum coated etalons have remained unchanged for over six months and have been used for interferometry down to 3000A. In the region 3000–4000A they are definitely superior to similar surfaces of silver.

I would like to thank Professor H. E. White for his advice and interest during this work.

NORMAN S. GRACE*
Department of Physics,
University of California,
April 6, 1933.

* Commonwealth Fellow.

Note on the Broadening of X-Ray Lines of Cold-Worked Aluminum

In the course of an investigation of internal strains in metals now in progress, the authors thought it advisable to check the experiments of van Arkel,[1] Dehlinger,[2] and others with regard to the reported impossibility of broadening the Hull-Debye-Scherrer lines of aluminum by cold-deformation, inasmuch as the effect of temperature of working seems to have been generally neglected in the work reported in the literature which has come to the authors' attention. In view of the kinetic nature of inner-strain-relief, the effect of working temperature seemed of theoretical interest, as the metals lead, tin, zinc and aluminum, which were reported to show no broadening of lines also have low recrystallization and melting temperatures.

A number of specimens of 99.97 percent pure aluminum were severely cold-worked by compression under similar conditions with the exception of temperature. The first group was compressed at room temperature, while the second was compressed in a bath of dry ice in acetone at −75°C.

The diffraction pictures, taken at room temperature, were completed within two hours after compression of the specimens, in order to minimize annealing effects. Moll microphotometer records were made of the (440) Fe $K\alpha$ doublet lines and the ratio of the maximum α_1 ordinate to the ordinate of the minimum between α_1 and α_2 was used as a measure of the sharpness of resolution. This ratio is 2.9 for the samples worked at room temperature, and 1.5 for those compressed at −75°C. Diffraction pictures of annealed specimens of aluminum have ratios for this doublet similar to that of the samples worked at room temperature. These results indicate that broadening of the x-ray lines of aluminum may be obtained by cold-working at −75°C.

L. Thomassen
J. E. Wilson

Department of Chemical Engineering,
University of Michigan,
April 7, 1933.

[1] A. E. van Arkel, Physica **5**, 208 (1925).
[2] U. Dehlinger, Zeits. f. Krystallographie **65**, 615 (1927).

Discontinuities of Magnetoresistance

According to current theories of magnetism a ferromagnetic body consists of small elements each magnetized to a saturation intensity J. The body as a whole will be unmagnetized unless a preponderance of the J vectors point in a given direction. An external field may magnetize the body by two possible processes: (A) reversal of the directions of those J vectors which oppose the external field, (B) rotation of the J vectors into the direction of the applied field. Process A is considered to be irreversible and process B is, in the main, reversible.[1] Barkhausen discontinuities of magnetization being irreversible, are on this view interpreted in terms of process A.

It has been found[2] that the magnetoresistance of nickel does not become very large (as the magnetic field is increased) until the magnetization curve of the nickel has passed the knee. Where the slope is greatest and where large Barkhausen jumps occur, the magnetoresistance is small and does not vary rapidly. W. Gerlach, therefore, supposes that process A does not affect the electrical resistance; magnetoresistance is due entirely to process B. He suggests[3] that "the irreversible phenomena are without influence on the electrical resistance, and therefore on the phenomena which exist in a rotation of Forrer's magnetic elementary bodies." Apparently these "irreversible phenomena" are the strikingly large jumps of magnetization discovered by Forrer.[4] An experimental test of this idea has been made as follows.

A nickel wire, 5 cm long, 0.01 cm in diameter, was bent into the arc of a circle and then thrust into a short length of capillary tubing. It was thus held straight but in a state of elastic strain. The tube and wire were then inserted in a small coil of about 3000 turns, connected through a three stage amplifier to a loudspeaker. When a permanent magnet was brought up slowly towards one end of the nickel wire the loudspeaker indicated the existence of one large magnetic discontinuity followed by several smaller ones. The search coil was now removed and the nickel wire connected in series with a rheostat and dry cell. The low-resistance side of a microphone transformer was put in parallel with the nickel wire, and the output side of the transformer connected to the amplifier and loudspeaker. With this arrangement a change, dS, in the resistance of the nickel will produce a change dI, in the current through the transformer, given by $dI=ERTdS/(RS+RT+ST)^2$, where E is the e.m.f. of the dry cell, R the resistance of cell and rheostat, T the resistance of primary of transformer, and S the resistance of the nickel wire. With a given nickel wire and transformer the condition for a maximum of dI is $R=ST/(S+T)$. This condition was approximately satisfied by adjusting the rheostat. When the permanent magnet was moved towards one end of the nickel wire in this circuit a sharp click was heard in the loudspeaker, followed by several smaller ones. These clicks were due to sudden changes of resistance corresponding to the magnetic discontinuities previously observed. (Unless some care is taken to adjust resistances and secure high amplification these clicks are of weak intensity. Also, the permanent magnet must not be brought too near the transformer or the Barkhausen effect of the transformer core will be heard.) Ordinary nickel or iron wire, when substituted for the strained nickel in the electric circuit produced noises in the loudspeaker very similar to the noise of the Barkhausen effect as picked up by the search coil.

We conclude, therefore, that discontinuities of resistance are associated with discontinuities of magnetization. It seems entirely reasonable that process A, mentioned above, should not produce any resistance change, because the resistance of a wire is unchanged by a mere reversal of its

saturated magnetism. For a similar reason it is hard to see why process A should produce any resultant magnetostriction. Since the Barkhausen discontinuities are found to be associated with both resistance jumps and magnetostrictive jumps[5] we must conclude that process A is not the main feature in the Barkhausen effect.

A third type of change which the J vector may undergo has been suggested.[6] This third process consists of a sudden swing of the J vector through 90° (in an unstrained cubic crystal) from one crystalline axis to another. If the Barkhausen effect is due to this kind of process it could have magnetoresistance and magnetostriction associated with it. Also, if process B is influenced by strains in the material it alone could give rise to jumps of magnetization, resistance, and magnetostriction in a manner previously described.[7]

C. W. HEAPS

The Rice Institute,
April 7, 1933.

[1] W. Gerlach, Ann. d. Physik **12**, 894 (1932).
[2] L. W. McKeehan, Phys. Rev. **36**, 948 (1930).
[3] W. Gerlach, Proc. Phys. Soc. **42**, 418 (1930).
[4] R. Forrer, J. de Physique **7**, 109 (1926).
[5] C. W. Heaps and A. B. Bryan, Phys. Rev. **36**, 326 (1930).
[6] W. L. Webster, Proc. Phys. Soc. **42**, 431 (1930).
[7] C. W. Heaps, Phys. Rev. **42**, 108 (1932).

Radiation Reaction Forces and the Expanding Universe

More than a year ago[1] the author pointed out that in a star that had just broken up, the reacting forces due to the asymmetrical radiation of mass would add momentum and kinetic energy to it, and it would be propelled through space much like a skyrocket.

An analysis of the motions imparted to a star as the result a deep seated thermal asymmetry resulting from fission shows that the kinetic energy W of an average star increases at a rate given by

$$\frac{dW}{dt}=\frac{Mf^2c^2b^2}{2}\left(\frac{1}{M}\frac{dM}{dt}\right)^2 t, \tag{1}$$

where M is the mass of the star, c the velocity of light, t the time and f and b are characteristic constants. A secular and statistical increase in the kinetic energies of all the stars implies an expansion of the system, and we have been able to work out, with sufficient completeness, the rate of expansion.

It is found that the radius of gyration of the galaxy is subject to a "uniform" acceleration (a) given by

$$a=\frac{2fbc}{[6/(1-q)]^{\frac{1}{2}}}\left(\frac{1}{M}\frac{dM}{dt}\right), \tag{2}$$

where q and dM/Mdt are supposed to be nearly constant. Now if G is the radius of gyration of a uniformly expanding system, then the velocity of recession V_r of a point at a distance R from an observer is

$$V_r=(dG/Gdt)R \tag{3}$$

and because of the form of Eq. (2) this becomes, to a first approximation

$$V_r=2R/\tau, \tag{4}$$

where τ is the interval of time since the Universe was comparatively dense. Putting Eq. (4) in terms of observed quantities we can show that

$$V_r=\frac{2^{\frac{1}{2}}fb(dM/Mdt)}{\Delta V/c}R. \tag{5}$$

The numerator can be evaluated from the masses, luminosities, etc. of the stars in the galaxy and the denominator determined from the observed differences in velocity ΔV between early and late type stars. With data that we believe to be correct, Eq. (5) becomes

$$V_r=10^{-17}R \tag{6}$$

and hence stars in our own galaxy must be statistically receding from us and at a rate proportional to their distance. The form of the equations show why the early type stars are observed to recede at the greatest velocity.

The mechanisms developed and applied to the galaxy are, with certain restrictions, applicable to nebulae. Eq. (6) is, of course, *identical in form and numerical constant with Hubble's observed relation.*

Our results indicate that the expansion is a slow evolutionary process and that the initial rate of expansion was probably small. The age of the Universe and galaxy approximates to 10^{10} years. We note particularly that we have not assigned special properties to space. Further, the expansion is real and results necessarily from radiation processes which take place in stars and nebulae that have suffered fission. Calculations show that except immediately after fission, the radiation reaction forces acting on a star are small compared to gravity and thus the motions of a star over short time intervals are adequately described by gravitational theory. But the mechanism slowly adds kinetic energy to the system and in describing the motions of stars over long periods of time, radiation reaction forces are perhaps of as great importance as the gravitational forces.

The complete papers should appear shortly.

ROSS GUNN

Naval Research Laboratory,
April 8, 1933.

[1] R. Gunn, Phys. Rev. **39**, 130 (1932).

Electronic Structures of Polyatomic Molecules and Valence. Magnetism of B_2H_6

In one of a series of articles under the above general title, begun in the Physical Review (1932–33) and hereafter to be continued in the Journal of Chemical Physics, it was stated that, on the basis of the method of molecular orbitals used in these articles, the interesting gas B_2H_6 is probably paramagnetic.[1] In one of the following articles in J. Chem. Phys. it will be shown that the structure of the molecule can probably be described by the electron configuration

$$(1s^2[\sigma_s]^2[\pi]^3)_2[\sigma_s+\sigma_s]^2,$$

in which the hydrogens in each BH_3 are bound to the B mainly by two $[\sigma_s]$ and three $[\pi]$ electrons, and the two B's are bound together mainly by the two $[\sigma_s+\sigma_s]$ electrons. The two latter may also contribute a little to the B–H bindings, and the six $[\pi]$ electrons more or less to the B–B binding.

If the interaction between the two $[\pi]^3$ groups should be strong, one could better write $[\pi+\pi]^4[\pi-\pi]^2$, using B_2H_6 orbitals instead of $[\pi]^3[\pi]^3$, using BH_3 orbitals. The types $[\pi+\pi]$ and $[\pi-\pi]$ are respectively bonding and antibonding for the boron-boron bond, and the whole group of six electrons would give a net bonding action between the two borons. In this case these six together with the two $[\sigma_s+\sigma_s]$'s are closely analogous to the eight electrons $(\sigma+\sigma)^2(\pi+\pi)^4(\pi-\pi)^2$,—usually written $\sigma^2\pi^4\pi^{*2}$ or $(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$,—which make the double bond in O_2. This set of electrons would give rise to three low-energy states $^3A_2$, ^1E, $^1A_1$ closely analogous to the three low states $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$ of O_2, with $^3A_2$ lowest analogous to $^3\Sigma_g^-$ of O_2. (It is assumed that the molecule has the symmetry D_3, but symmetry D_{3h} or D_{3d} would give essentially the same states.) B_2H_6 should then be paramagnetic like oxygen.

More probably the interaction between the two $[\pi]^3$ groups is weak, in which case, it can be shown, B_2H_6 should have a group of six low-energy states $^3A_2$, ^1E, $^1A_1$, $^1A_1$, ^3E, $^3A_2$ close together. Very likely a $^3A_2$ would still be the lowest as in the other limiting case, but even if this should not be true, a $^3A_2$ and a ^3E state must lie sufficiently close to the lowest state to be considerably populated at room temperature and so to make B_2H_6 paramagnetic. Since paramagnetism is thus predicted in both limiting cases, the same prediction is very likely, although not certain, to hold good for intermediate cases. Since, however, the actual case is probably near the second limiting case, it may be predicted with some confidence that B_2H_6 is actually at least weakly, but probably strongly, paramagnetic. If, however, B_2H_6 should prove to be diamagnetic or only weakly paramagnetic at room temperature, it may be expected to become more strongly paramagnetic on raising the temperature.

ROBERT S. MULLIKEN

Ryerson Physical Laboratory,
University of Chicago,
April 10, 1933.

[1] R. S. Mulliken, Phys. Rev. **41**, 756 (1932).

On the Plasticity of Crystals

A. Smekal[1] recently in a letter to *The Physical Review* is still advocating the idea that microscopic crevices are the essential cause of the peculiar mechanical and plastic behavior of rocksalt and crystals in general. Although conclusive evidence has repeatedly been brought forth by myself and other writers that Smekal's "imperfection" theory does *not* account for some of the most essential physical properties of crystals, his remarks in the mentioned letter require some comment.

In the first place the postulate of microscopic crevices does not account for the fact that the strength of good, pure crystals against gliding is consistently of the order of one-thousandth of what one would expect for ideal lattices. If the crevices are, as Smekal states, of an *accidental* nature and if they are therefore irregularly distributed and of various sizes, they will cause a *wide spread* in the values of the strength against slipping for different specimens. Furthermore, it is known that the more imperfect (deformed, contaminated) a crystal is, the more its strength approaches values which one would really expect for the ideal crystal; and the more perfect a crystal is experimentally the smaller is its strength as compared with the strength an ideal crystal should have. This paradoxial behavior of real crystals is therefore exactly contrary to Smekal's theory.

Secondly, Smekal's ideas *do not account* for the *fundamental fact*, that the strength against slipping at higher temperature is *independent* of the temperature, retaining a constant finite value over a considerable range of temperatures until the crystal melts abruptly and the shearing strength drops to zero. If crevices determined the shearing strength it would vary greatly with temperature, because the thermal energy of the crystal is of the same order of magnitude as the potential energy changes involved in widening or closing the crevices by a deformation of the crystal. It is not permissible, as Smekal has done, to explain the invariance of the strength against temperature changes by comparing the thermal energy with the total energy of an atom in the crystal. Indeed the energy of deformation is only a very small fraction of the total potential energy and is therefore quite comparable with the total thermal energy. The "imperfection" theory also has never accounted for the fact that the strength against shear is strongly dependent upon temperature for low temperatures although it assumes a constant value for higher temperatures.

In the third place some of the phenomena, *predicted* by the theory of the secondary structure and found experimentally by Mr. Hasler, myself, A Goetz, A. Straumanis and F. Bitter, are *inconsistent* with Smekal's postulate of "Lockerstellen" (regions of loosely bound atoms). These effects are the following ones. The theory of the secondary structure requires that the distribution of matter, or energy in a crystal be represented by a triple Fourier series with at least two periods or two lattice constants, d and

$D \gg d$ which are characteristic for the primary and the secondary structure, respectively. The theory claims in the first place that the spacing D of the secondary structure is essentially independent of the conditions under which the crystals are grown. This is actually true for the secondary patterns which have been observed on Bi, Cd, Zn and especially for the magnetic secondary structure on magnetized crystals of Fe and Ni as observed by F. Bitter. The theory in the second place predicted that etching or evaporation would attack first the atoms in the center of the secondary blocks. This has been verified also and proves conclusively that the observed secondary patterns *cannot* be systems of slip lines as Smekal thinks. If they were slip lines their higher energy content naturally would favor etching or evaporation, so that instead of obtaining definite (triangular, etc.) etching grooves a system of long grooves would result. The fact that the outlines of the patterns observed by us offer a considerably greater resistance against etching than the apparently ideal parts I regard as a conclusive confirmation of the postulate of a secondary structure.

Finally a powerful esthetic argument may be advanced against the theory that imperfections are the cause of all the structure-sensitive properties of crystals. Indeed during the ten years of its existence nobody has been able to derive from this theory *any quantitative* description of the structure-sensitive properties of crystals. The theory of the secondary structure on the other hand provides for a quantitative understanding of the whole complex of peculiar mechanical properties of crystals as will be shown by the author in a forthcoming publication in *The Physical Review*. This theory also gives a satisfactory answer to the question why crystals exist at all and accounts for the heat of fusion, for the sharpness of the melting point and for cooperative volume effects in crystals. The postulate of the secondary structure therefore can be regarded as a more satisfactory working hypothesis than the conception of imperfections in crystals.

Smekal in his paper quotes the criticism which E. Orowan[2] recently published against the theory of the secondary structure. E. Orowan claims to have made more accurate calculations than the author. This accuracy, however, is obtained at the price of deliberately disregarding some very essential effects which I have introduced into my calculations and which cannot be omitted. Mr. Orowan's criticism consequently is based on entirely impossible premises. For details I must refer the reader to my related article on the physics of real crystals appearing in the *Helvetica Physica Acta*.

The particular problem of the influence of water on the plasticity of rocksalt which Smekal discusses can be satisfactorily treated only after the plastic properties of pure NaCl crystals have been quantitatively understood. As A. Smekal has not advanced any such theory his discussion is necessarily premature and unfounded.

F. ZWICKY

California Institute of Technology,
Pasadena,
April 10, 1933.

[1] A. Smekal, Phys. Rev. **43**, 366 (1933).
[2] E. Orowan, Zeits. f. Physik **79**, 573 (1932).

Band Spectrum of CS

Martin[1] obtained a spectrum attributed to CS in the region λ2418 to λ2854. We have photographed this band spectrum from a number of discharge tubes at both high and low dispersion, with the result that a total of some 170 heads, about one hundred of them new, have been recorded, extending from λ2400 to λ3330. The new bands fall into the vibrational array given by Jevons[2] extending the vibrational quantum numbers to $v' = 11$ and $v'' = 16$.

The strongest of the CS bands have been successfully photographed in the third order of a 21-ft. grating (dispersion of 0.66A per mm), the Q and P branches being clearly resolved to the origin. The majority of the bands have single P, Q, R branches, and are hence due to $(^1\Pi \rightarrow {}^1\Sigma)$ or $(^1\Sigma \rightarrow {}^1\Pi)$ transitions, as inferred by Jevons. Provisional values for the moments of inertia are $I' = 37.3 \times 10^{-40}$ and $I'' = 35.1 \times 10^{-40}$ gram cm^2, a difference of about 6 percent. This is in good agreement with the results for the band system of AlO. Results of this analysis will be reported at a future date.

F. H. CRAWFORD
W. A. SHURCLIFF

New Research Laboratory,
Harvard University,
Cambridge, Massachusetts,
April 11, 1933.

[1] Martin, Proc. Roy. Soc. **A89**, 127 (1913).
[2] Jevons, Proc. Roy. Soc. **A117**, 251 (1928).

Lack of Observed Hyperfine Structure in Strontium

Strontium has been stated by Aston to have three isotopes of mass 88, 86, and 87 of abundance respectively 83.3, 10, and 6.6 percent. Isotope 87 might be expected to show spin hyperfine structure. It is also possible that such structure could arise from isotopes 88 and 86 and structure because of isotopic displacements might be found in the strontium spectrum. The resonance lines of Sr II, λ4215.5 $(5\,{}^2S_{\frac{1}{2}} - 5\,{}^2P_{\frac{1}{2}})$ and λ4077.7 $(5\,{}^2S_{\frac{1}{2}} - 5\,{}^2P_{\frac{3}{2}})$ were examined by Frisch[1] in the fourth order of 21 ft. grating and reported sharp, with a half-width in the case of λ4077 of 0.20 cm^{-1}. Murakawa[2] in a paper on the h.f.s. of barium reproduces a plate of λ4215 made with 1 cm Lummer-Gehrcke plate which seems to show a strong central component with an unresolved fainter component on either side. The description states that "the doublet separation of Sr^{87} is about 0.140 cm^{-1}." This is not neces-

sarily in conflict with Frisch's result since his half-width was given as 0.20 cm^{-1}. Using a hollow cathode discharge and a Fabry-Perot etalon with separations of 12 and 19 mm we have examined some forty lines of Sr I and Sr II in the region λ5600–4000 and find no evidence of any hyperfine structure in any of the lines. In particular λ4215 examined under a considerable variety of current densities and exposure times shows no evidence of the components photographed by Murakawa although our total fringe width is approximately 0.08 cm^{-1}. It is of course true that the components if due to Sr^{87} should have together only 6 percent of the intensity of the central component and might be overlooked on an underexposed plate. However the Ba II lines λ4934 and λ4554 appeared as impurities on our plates and the weak components of these lines believed to be due to the odd isotope Ba^{137}, whose abundance is 11 percent, are well developed. Sr I lines which should be favorable for the observation of h.f.s. are λ5257 ($5s\,4d\,{}^3D_3-4d\,5p\,{}^3P_2$) and λ5481 ($5s\,4d\,{}^3D_3-4d\,5p\,{}^3D_3$) which are the strongest lines in their respective multiplets. These lines should have sharp upper terms and well separated lower terms. The two lines, however, like several others observed in the same multiplets, appear perfectly sharp and with fringe widths of approximately 0.10 cm^{-1} each. Incidentally the two analogous Ba I lines, λ6111 and λ6499, each show definite h.f.s. according to unpublished measurements by R. Ritschl and one of us (R.A.S.). The two strontium lines just discussed should also be favorable for the detection of isotope shifts since in each case one term only has a penetrating *s*-electron. Another line which has been examined as favorable to the observation of an isotope shift is λ4607 (Ba I $5\,{}^1S_0-5\,{}^1P_1$), but it also appears perfectly sharp with a fringe width of about 0.13 cm^{-1}. Our conclusion is that strontium has no nuclear spin h.f.s. or isotope shift greater than 0.050 cm^{-1}.

A. N. BENSON
R. A. SAWYER

University of Michigan,
Ann Arbor, Michigan,
April 11, 1933.

[1] Frisch, Zeits. f. Physik **71**, 89 (1931).
[2] Murakawa, Tokyo Inst. Phys. Chem. Res. **18**, 305 (1932).

The Continuous Beta-Ray Spectrum

The idea that mass and energy are equivalent has been of the greatest importance in helping to unravel the processes occurring in disintegration problems. Although this concept has been tested in many different ways, the continuous beta-ray spectrum has thrown some doubt on its validity when applied to the changes undergone by an electron in the formation of a beta-particle. In this process, the electron has certainly suffered a radical change in its properties, a change which must have been accompanied by just as great a readjustment of the stresses (non-Maxwellian in origin) which give the electron its identity. The question then arises whether or not the energy associated with these non-electromagnetic stresses has an equivalent mass. However, we should expect the law of the conservation of energy to be always valid.

Kaluza and O. Klein have developed a geometrical interpretation of the equation of motion of charged particles. This has been extended by Flint[1] by the introduction of the idea of Weyl that the length l of a vector A depends on the value of the electromagnetic field. He derives an expression for the length

$$l^2=\gamma_{mn}A^mA^n=l_0^2\exp\left[-(2\pi i/h)\int mcdx^5\right],$$

which varies periodically with a frequency mc/h. Schrödinger in a paper on the motion of a free particle shows that an internal oscillation of this same frequency is present.

Both these investigations are based, however, on the supposition that the properties of the electron are fixed. In the incipience of a beta-particle in radioactive decay, on the other hand, the electron's properties are in a state of flux. For example, the rest mass seems to change from practically zero to its final value as the electron leaves the nucleus. In such a case, the mass m will be a function of the coordinates of the path by which the electron leaves and the length of a vector associated with the path will depend on the value of the integral $\int mcdx$, whose final value depends on the path of integration.

In the formation of a beta-particle from the nuclear electron, the amount of energy required to build up the non-electromagnetic stresses may not be independent of the way in which these stresses arise. The variation of the electromagnetic energy of the beta-particle would thus be accompanied by a corresponding variation of the energy of the nuclear stresses but if this latter does not manifest itself as electromagnetic mass we would have no means of detecting it. In any case in which the rest mass of the electron changes we might not expect the law of the conservation of mass to apply. The tentative suggestion, that for the same rest mass of the nucleus, the energy of the nuclear stresses may be different depending on the method of building up these stresses, must be decided by further work.

These ideas are based on the supposition that the masses of all the nuclei of the same constituents have the same mass—we are not here considering the small difference which might arise from the nuclear entities not having the same configuration and hence not the same mass in the same way that in the atomic system, the energy levels of the atom in the ground state may differ by a small amount.

ARTHUR BRAMLEY

Bartol Research Foundation of
The Franklin Institute,
Swarthmore, Pennsylvania,
April 11, 1933.

[1] Flint, Proc. Roy. Soc. **A131**.

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. Giauque
D. P. MacDougall

Department of Chemistry,
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Berkeley, California,
April 12, 1933.

The Equilibrium Theory of the Abundance of the Elements

It is possible by the theory whose development was announced[1] in a previous letter to calculate, for assemblies in which there is equilibrium regarding nuclear transmutations, not only the abundances of the elements but also the pressures and energies. One may draw conclusions from the theory concerning the fashion in which energy must be liberated in the stars by transmutations of nuclei, if the equilibria are there established. There is good reason for believing that these equilibria are in fact established inside of many stars, if not within all stars.

One immediate conclusion from the theory is that if all nuclei are composed ultimately of electrons and protons, then the most abundant element when equilibrium is established—for densities greater than 1 g/cm³ and less than 10^6 g/cm³, and at temperatures which are not too high—must usually be the element of even mass number and smallest packing fraction. The packing fraction of Fe^{56} has not yet been measured so far as I am aware, but it lies close to the bottom of Dr. Aston's curve of packing fractions; if $iron^{56}$ has really the smallest packing fraction of all the "even" elements, then the abundance of iron in the stars, its great preponderance in many meteorites and its probable abundance inside of the earth can all be understood.

If a certain region in a star in which these equilibria are established is maintained at strictly constant temperature, then there can be no "generation" of energy by transmutations. If, however, the region cools at a rate so slow that the equilibria at any one instant are nearly perfectly established, energy will be liberated by the transmutations at a rate which can be calculated. The rate of liberation of energy is then proportional to the rate at which the region is cooling, among other things. The rate of liberation of energy, and the abundance of the elements, require for their computation a knowledge of the packing fractions of all of the isotopes of all the elements, the levels of nuclear excitation, and the spins of the nuclei in their normal and excited states.

The theory in the form of two detailed papers has been communicated to the Royal Astronomical Society, since it is considered that the *Monthly Notices* of that society is perhaps the most suitable place for the publication of the theory.

T. E. Sterne,
National Research Fellow.

The Jefferson Physical Laboratory,
Cambridge, Massachusetts,
April 13, 1933.

[1] T. E. Sterne, Phys. Rev. **43**, 585 (1933).

Surfaces from which Cold Emission Currents Appear Only at Very High Field Gradients

With a thoriated tungsten filament as the wire at the axis of a carefully shielded cylinder, currents were drawn from the wire after giving it various heat treatments. Curve *A* in the figure represents the current from the wire after it had been heated in the baking-out process during which the furnace was kept at 450°C for twenty-four hours and the plates were heated to a bright red by means of an induction furnace. The wire was then heated to 2000°K for thirty minutes after which curve *B* was obtained. The filament was again heated, this time to a temperature of 2900°K for thirty minutes after which treatment no measurable current appeared until the field was raised to 3.5×10^6 volts per cm at which potential gradient the current seemed to rise spontaneously from no measurable value to a current of the order of 10^{-4} amperes. A distinct glow accompanied this current. After this rise in current the curve *D* was taken without any further treatment. A rapid rise and the subsequent current curve at a lower potential gradient was reported by Bennett.[1] The wire was then heated to 2800°K for approximately one minute. This treatment shifted the curve to the position *E*. Bennett observed these break-

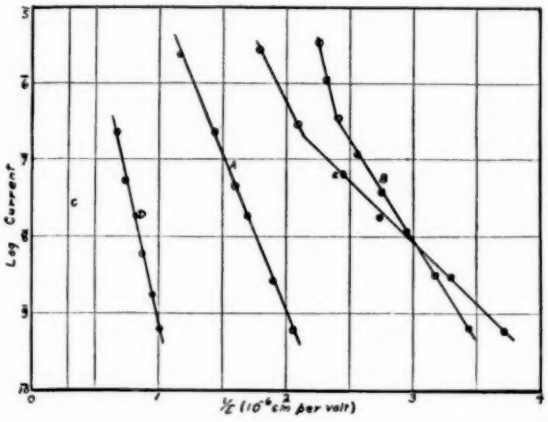

FIG. 1.

downs from unconditioned electrodes at calculated potential gradients far below the values obtained by the writer. Several observations of this breakdown phenomenon were observed. The breakdown never occurred below a potential difference of 10,000 volts although in some instances part of a field current curve came in the measurable range before the breakdown occurred. The point at which breakdown occurs seems to be a function of both the current and the potential difference.

In order to show whether or not the change in emission after the breakdown is due to a change in the work function, the work function was measured before and after the breakdown. This measurement showed that there was no change to an accuracy of fifteen percent.

C. C. CHAMBERS

Bartol Research Foundation of
The Franklin Institute,
Swarthmore, Pennsylvania,
April 13, 1933.

[1] Bennett, Phys. Rev. **37**, 583 (1931).

Double-Refraction Effects in the Kennelly-Heaviside Layers

Recent improvements in experimental technique have stimulated interest in the "fine structure" of the records produced by radio waves which have been refracted in the upper levels of the atmosphere. Numerous observers have noted the "split echoes" which apparently result from magneto-ionic double-refraction in the high layer. Rukop and Wolf[1] have presented typical continuous records, showing the customary slow separation of the components as the electron density falls during the night, and the rapid merging of the echoes during the normal sunrise effect. Eckersley[2] and Appleton[3] report experimental verification of the hypothesis that the two rays are circularly polarized in opposite senses. During the past year we have taken a large number of automatic photographic records over 24 hour periods, and have recorded continuously (for more than 2100 hours) since January 1, 1933. In addition to the normal effects which we have previously described,[4] we have investigated many abnormal records produced by magnetic storms and other disturbing factors. During disturbed conditions we often find that the curves intersect at an angle, as if the ordinary and extraordinary ray were rapidly exchanging places. A slower exchange was noted in our record of the September, 1932, eclipse.[5] Magnetic variations may cause observable double-refraction at any hour of the day, but the effects seem to be especially violent when the electron density is small. An extreme case is presented in Fig. 1. The apparent presence of a *third* component in the first order reflection has been noted in other cases. The dotted lines represent normal behavior on an undisturbed day. The pulses were sent by a transmitter operated by Tufts College at a point about 14 kilometers north of our laboratory. The frequency was 4095 kilocycles.

The use of continuous automatic recorders permits the comparison of our data with observations made simultaneously in other parts of the world. Some of our 1932 curves coincide in date with the records recently presented by Rukop and Wolf.[1] For example, Wolf comments on the strong multiple reflections from the low layer which

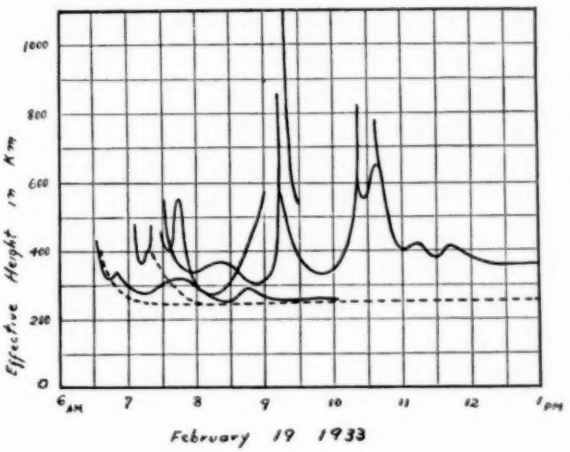

FIG. 1.

appeared several hours before sunrise June 10, 1932. Similar effects were noted in Cambridge, and were reported at the June meeting of the Physical Society. This sort of

[1] H. Rukop and P. Wolf, Zeits. f. tech. Physik **13**, 132 (1932); P. Wolf, Hoch:tech. u. Elek:akus. **41**, 44 (1933).

[2] T. L. Eckersley, Nature **130**, 398 (1932).

[3] E. V. Appleton and J. A. Ratcliffe, Nature **130**, 472 (1932).

[4] H. R. Mimno and P. H. Wang, Phys. Rev. **41**, 395A (1932).

[5] H. R. Mimno and P. H. Wang, Proc. I. R. E., April, 1933.

correlation is decidedly useful and should be extended. A detailed report will be presented later.

Mr. J. F. Herd[6] has described a synchronized "grid-blocking" transmitter, recently developed by the (English) Radio Research Board for sending the short pulses which are used in echo measurements. This is the circuit which we used in field measurements last summer, and described at the October meeting of the Institute of Radio Engineers in Cambridge. We have no desire to claim priority, or to dispute the usefulness and convenience of the circuit for the "Polar Year" work. However, the inherent frequency-modulation, produced by this simple type of modulated oscillator, renders it unsuitable for extensive use in the crowded channels now encountered in America, and we hope that it will not be generally adopted here. We have prohibited the use of this device in our own laboratory since October, as it is quite possible to use circuits which will produce less interference with other important services.[7] The transmitter should have frequency stability, the pulse length should be readily controllable, and should not be unnecessarily short. A description of our present apparatus will soon be offered for publication.

HARRY ROWE MIMNO
P. H. WANG

Research Laboratory of Physics,
Harvard University,
April 19, 1933.

[6] J. F. Herd, Proc. Phys. Soc. (London) **45**, 221 (1933).
[7] H. R. Mimno and P. H. Wang, Phys. Rev. **48**, 501A (1933).

Band Spectrum of the H^1H^2 Molecule

The spectrum of the H^1H^2 molecule has been photographed in emission in the first order of a 21 foot grating. The bands of H^1H^2 corresponding the $H\alpha$ bands of H_2 have been measured. The Q branches have been found in considerable intensity in all of the bands measured up to the present time—namely the 0″–0′, 0″–1′, 1″–1′, 1″–2′. The R lines have been identified up to $R=4$ for the 0″–0′ band. The order of intensity Q, R, P is the same as the H_2[11] molecule for the $H\alpha$ bands.

The rotational and vibrational isotopic shifts check the calculated values to within the accuracy of the present preliminary calculations and measurements. RP combinations have been used to check the rotational levels of the $^3\Sigma$ lower state. An electronic isotopic shift of about 2.4 wave numbers has been observed.

More than 300 new lines have been observed in the limited region studied and a more detailed analysis will be carried out. This investigation is preliminary to a study of the nuclear spin of H^2, from an analysis of the H^2H^2 bands, undertaken in collaboration with Professor G. N. Lewis, who has provided the high concentration of hydrogen isotope used in the present work.

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April 17, 1933.

Search by Deflection-Experiments for the Dirac Isolated Magnetic Pole

The recent discovery of a positively charged particle of e/m similar to that of the negative electron, presumably related to the positive electron predicted by Dirac, perhaps justifies calling the attention of other experimentalists briefly to the possibility of detecting the existence of single isolated poles, as predicted by Dirac,[1] by proper deflection-experiments with magnetic or electric fields, most conveniently the former. Simple calculations made by the writer more than a year ago, in connection with Richardson's[2] suggestion of a possible relation of such isolated magnetic poles to phenomena of the penetrating radiation, indicated that with reasonable assumptions as to its mass such a single pole having a kinetic energy even as great as 10^8 electron-volts should have a path of appreciable curvature in an apparatus similar to Anderson's,[3] but this curvature, being at right-angles to that of an electrically charged particle, would not be observable with the camera axis parallel to the magnetic field, even if such a high-speed isolated magnetic pole should be an ionizing particle. No high-energy deflection-experiments reported to date would have detected such a phenomenon, with the possible exception of the recent experiments of Blackett and Occhialini[4] who used stereoscopic cameras.

By Dirac's Eq. (9) the magnetic charge on a one-quantum pole should be $\mu=hc/2e$, where μ is in magnetic units, e in electrostatic units, and h is Planck's constant divided by 2π. The force on such a one-quantum isolated magnetic pole in a magnetic field of one gauss is then 3.28×10^{-3} dyne. This is nearly 70 times the force on an electron in unit electrostatic field, and similarly 70 times the transverse force on an electron of $v\leqq c$ moving in a magnetic field of unit strength. If these single poles are contained in the structure of the nucleus, their dimensions must be of the order of nuclear dimensions. They must then be comparable to the electron in size; hence their (potential) energy and rest-mass must be at least as great

[1] P. A. M. Dirac, Proc. Roy. Soc. **A133**, 60–72 (1931).
[2] O. W. Richardson, Nature **128**, 582 (1931).
[3] C. D. Anderson, Phys. Rev. **41**, 405–421 (1932).
[4] P. M. S. Blackett and G. P. S. Occhialini, Proc. Roy. Soc. **A139**, 699–726 (1933).

and probably considerably greater than that of the electron. Even if the mass is $(70)^2$ as great, the force on such a unit-pole being 70 times that on a fast-moving electron in the same magnetic field, the path-curvature is consequently still roughly comparable, especially when relativity considerations are taken into account. Langer gives the figure for the mass as $1/4\alpha^2 = 4700$ times that of the electron and Richardson gives the rough factor 500 times the mass of the electron.

Since it is improbable that such a high-speed isolated magnetic pole would have the same type of interaction with atomic structures as high-speed electrically charged particles, perhaps the most promising direction for observational attention is that of the "non-ionizing links" referred to by Blackett and Occhialini, and of similar non-ionizing connections giving rise to nuclear phenomena in "neutron" experiments and very likely to be expected in high-voltage nuclear disintegration experiments. In addition, of course, the behavior of unusual highly ionizing particles should be scrutinized to insure that their identity is correctly established. One experiment adapted to the detection of such high-energy isolated magnetic poles has been a part of our projected program for some time, waiting on the acquisition of a magnet of suitable dimensions. Other tests requiring smaller magnetic fields and dealing with a lower energy region are being undertaken.

M. A. TUVE

Department of Terrestrial Magnetism,
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Washington, D. C.,
April 17, 1933.

A Nitrogen Disintegration by a Very Fast Neutron

I have recently photographed in nitrogen a very remarkable disintegration fork caused by a beryllium neutron. If conservation of momentum be assumed, the energy of the incident neutron may be computed from the lengths of the times of the fork and the angle between them to be $17(10)^6$ volts. This is greatly in excess of the energies attributed to neutrons by Chadwick or I. Curie and F. Joliot, and may be compared with the $16(10)^6$ volt neutron reported by Harkins, Gans and Newson.[1] The peculiarity of this fork which is so marked is that it is due to a neutron which owed its origin to beryllium being bombarded by α-particles from *polonium*. The maximum energy which may be released in these circumstances is $(Be^9 + He^4 - C^{12} - n^1) + E^\alpha$. The energy set free by the mass-change is $6.9(10)^6$ volts and E^α for polonium is $5.4(10)^6$ volts, a total of $12.3(10)^6$ volts. The discrepancy, amounting to $4.7(10)^6$ volts, cannot be due to experimental error, since the fork is a good one and may be accurately measured. The probable error is not over $(10)^6$ volts in the energy of the neutron.

This particular fast neutron is not generous with its great energy: the recoiling nucleus (B^{11}) and disintegration particle (He^4) are of ordinary energies. The "loss" in energy amounts to $13.6(10)^6$ volts. This could possibly be accounted for by allowing the creation of a slightly heavier B^{11} than one measured in the mass-spectrograph. The excess weight due to complete absorption of the $13.6(10)^6$ volts would be too slight to be observable.

FRANZ N. D. KURIE

Sloane Physics Laboratory,
Yale University,
April 19, 1933.

[1] W. D. Harkins, D. M. Gans and H. W. Newson, Phys. Rev. **43**, 584 (1933).

New Lines in the Electronic Band Spectrum of Neutral OH

By the use of high-frequency excitation and a very rapid flow of water vapor through the tube, the general background radiation obtained in photographing the electronic band spectrum of water vapor has been greatly reduced. As a result, it has been possible to bring out various faint lines not previously reported that lie on the short wave-length side of the 3064 (0, 0) band. The very high initial purity of the water and the repeated distillations while in use served to produce a spectrum entirely free from any trace of either carbon monoxide or nitrogen. It therefore seems justifiable to consider that the faint lines found are due to water vapor and not to impurities.

Nine of the lines lie between the lines of the $^{RR}R_{21}$ branch of the 3064 band which lies just beyond the main band head on the high-frequency side. Four of these are evidently additional lines of this branch. The remaining five agree well with the computed values of the $^{RR}R_{21}$ branch of the isotope OH in which H has an atomic weight of 2 and it is suggested that they may be due to this cause. The lines cannot be additional members of the main $^{RR}R_{21}$ branch as their frequencies do not check with the computed frequencies of these. This region would appear to be more favorable for the observation of possible isotopic lines than any other as the corresponding main lines are quite strong and the region in which the isotope lines should fall is sufficiently free from other lines to make observation of a number of them possible with a Hilger E-2 quartz spectrograph. The use of an instrument of greater dispersion would appear inadvisable because of the faintness of the lines.

The diagram shows the relative positions of the $^{RR}R_{21}$ branch of the 3064 band, our new lines, and the calculated position of the isotope $^{RR}R_{21}$ branch. The five lines nearest the band head would be unresolved with the dispersion

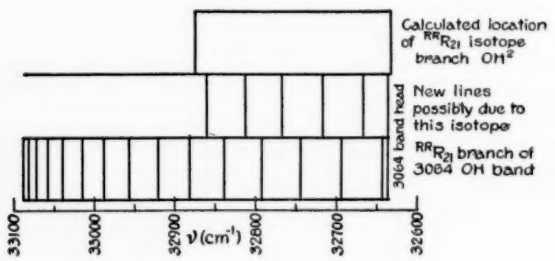

FIG. 1.

used, 5.76A per mm which would account for the fact that we find only one line corresponding to the band head. Lines are found that agree well with the computed positions of all the others that do not fall too close to a main branch line to be observed. Further work is in progress to establish more definitely whether these lines are due to OH^2.

At the head of the 2608 band a series of singlet lines has been found corresponding to the $^{RR}R_{21}$ branch discovered by Watson for the 3064 band, by Jack for the 2811 band and by Johnston and Dawson for the 3122 band. Two additional groups of about twelve lines each are found at still shorter wave-lengths the locations of which indicate that they may represent portions of the (3, 0) and (4, 1) OH vibrational bands.

This work is being done in the Physics Laboratory of the University of Michigan.

KATHERINE CHAMBERLAIN
HAROLD B. CUTTER

Departments of Chemistry and Physics,
Colleges of the City of Detroit,
April 19, 1933.

Proceedings of the American Physical Society

MINUTES OF THE NEW YORK MEETING, FEBRUARY 24–25, 1933
JOINT MEETING WITH THE OPTICAL SOCIETY OF AMERICA

THE 183rd regular meeting of the American Physical Society was held in New York City on Friday and Saturday, February 24–25, 1933, as a joint meeting with the Optical Society of America. The presiding officers at the sessions of the Physical Society were Dr. Paul D. Foote, President of the Society, Professor Arthur H. Compton, Vice-president, Dr. Karl K. Darrow, Dr. W. E. Forsythe and Professor John Zeleny. All sessions were held at Columbia University in the Physics Laboratories.

The joint session with the Optical Society of America was held on Friday afternoon at two-thirty o'clock. This session was a symposium on "Electron Optics." The President of the Physical Society, Dr. Paul D. Foote, presided. The invited papers were as follows: *Electron Optics* by C. J. Davisson, Bell Telephone Laboratories, Inc.; *Diffraction of Low-Speed Electrons* by H. E. Farnsworth, Brown University; *A Lens for Cosmic-Ray Electrons* by W. F. G. Swann and W. E. Danforth, Jr., Bartol Research Foundation; and *On Electron Beams in High Vacuum* by Vladimir K. Zworykin, RCA Victor Company. The attendance at this symposium was about three hundred and fifty.

One hundred and sixty-five persons attended the luncheon at the Columbia University Faculty Club on Friday.

On Friday evening the Society joined with the Optical Society for dinner at the Hotel New Yorker. This dinner was attended by ninety guests. The President of the Optical Society, Dr. E. C. Crittenden, presided. The after dinner speakers were Dr. Paul D. Foote, Dr. L. B. Tuckerman and Professor Harold C. Urey.

Meeting of the Council. At its meeting on Friday, February 25, 1933, the Council elected thirty-three candidates to membership. *Elected to Membership:* Stanley S. Ballard, John F. Byrne, François Canac, Joseph F. Carroll, Lyman Chalkley, Jr., Don E. Davidson, Grant O. Gale, Max Goodrich, Cecil E. Haller, Sidon Harris, Sterling M. Heflin, N. P. Heydenburg, Roger W. Hickman, James L. Hoard, Waldo H. Kliever, John C. McDonald, D. M. Morandini, Wilson C. Morris, Harald Norinder, Austin J. O'Leary, Eugene W. Pike, Martin Rusch, Richard E. Smith, Hirsh W. Sulkowitch, Tikawo Tamura, Lauriston S. Taylor, C. Irwin Vigness, John P. Vinti, W. H. Wells, Benjamin F. Wissler, Robert C. Woods, Fumio Yamasaki and Walter H. Zinn.

The titles and abstracts of papers presented before the Optical Society of America will be found in the Proceedings of that Society, published in the Journal of the Optical Society.

The regular scientific program of the American Physical Society consisted of forty-three papers, numbers 29, 32, 33 and 37 were read by title. The abstracts of these papers are given in the following pages. An *Author Index* will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Influence of the Dielectric Constant of the Medium on the Potential and Charge of a Protein Surface in a Liquid. HAROLD A. ABRAMSON, *Columbia University and* JANET DANIEL, *Harvard University.*—If the electric mobility of microscopically visible quartz particles covered with a film of adsorbed protein is studied in different concentrations of alcohol, it is possible to correlate the surface potential and surface charge calculated from these mobilities with the charge obtained by another (thermodynamic) method. The results indicate that the character-

ization by the two parameters viscosity and dielectric constant of the solvent in the Helmholtz-Debye theory is correct. This is in accord with the views of Frivold, Halpern, Gross and others who have investigated theoretically the effect of lowering the dielectric constant. The data are interpreted from the point of view of their biological importance particularly in connection with the problems of cell permeability.

2. A Vacuum Tube Instrument for Measuring Very Small Unidirectional Currents and Voltages. G. FAILLA, *Memorial Hospital, New York.*—In the "floating grid" vacuum tube device for measuring ionization currents, described by the author (Radiology, Oct. 1930), the current to be measured is "balanced" by another ionization current, whose magnitude is easily determinable. With such a device there is a lower limit for the magnitude of the current which can be detected, no matter how high the voltage producing the current may be. Similarly, there is a lower limit for detectable potential difference, irrespective of the magnitude of the current which the source might be able to produce. The current sensitivity of the device may be increased by charging a condenser for a certain time and then discharging it to the grid of the vacuum tube. The value of the current is determined by measuring directly the voltage to which the same condenser must be charged to give the same "ballistic" deflection of the plate circuit meter. The procedure for the measurements of small voltages is similar, except that the condenser capacity is decreased before discharging it to the grid.

3. A New High Tension Electrostatic Voltmeter. J. E. SHRADER, *Drexel Institute, Philadelphia.*—Several years ago the author devised an electrostatic voltmeter operating on the principle of electrostatic repulsion between stationary vanes and a set of vanes carried by a torsional suspension. The instrument was calibrated by observing with a lamp and scale the deflection of a spot of light from a mirror attached to the movable vane when known voltages were applied. This instrument proved quite reliable but had the disadvantage of not being self-contained. The present instrument is also quite reliable and is self-contained. The instrument consists of a movable plate hinged or held by a thin flat spring in a horizontal position parallel to a similar plate carried on the end of a rod carried by an insulating bushing inside a vessel containing transformer oil as an insulating medium. Upon the application of potential the movable plate will be repelled downward. Attached to the movable plate is a small glass rod extending horizontally to the extreme end of which is fastened a fairly strong silk string. This string extends upward and is wrapped about a small spindle and is held under tension by a light spiral spring at the top of the vessel. When repulsion between the vanes takes place the spindle is caused to rotate and the amount of rotation is indicated by the motion of a pointer on the end of the spindle and this motion on a circular scale is observed through a circular window on the instrument. The sensitivity is determined by the weight and stiffness of the movable vane, by the diameter of the spindle and the length of the pointer and by the stiffness of the controlling spring. For greater insulation the vessel is lined with insulating material such as fullerboard which serves as a baffle to prevent discharges to the grounded vessel.

4. High Voltage X-Ray Tube and Constant Potential Transformer Equipment. CYRUS A. POOLE AND W. S. WERNER, *Kelley Koett Mfg. Co., Covington, Kentucky.*—This is a preliminary report on the design, construction and operation of a porcelain insulated, grounded anode x-ray tube to operate at 800,000 volts constant potential. This is a hot cathode tube with water-cooled anode. A pressure of 10^{-5} or better is maintained by continuous pumping with a two-stage diffusion pump, backed by "Megavac" oil pump. Power is furnished to this tube by a Cascaded system of transformer units, with the condenser filtered La Tour circuit in each unit. The output is a constant potential direct current, having practically no ripple. Corona and secondary currents are discussed. Although high-voltage tubes have been operated at this potential before, none have been built prior to this to operate on constant potential direct current. Since all the energy is supplied at the peak voltage the output rays are comparable in frequency to gamma-rays and their intensity far exceeds the aggregate intensity of all available radium. In addition to this, the high-voltage power unit is of special interest since it can be utilized in other types of research where high voltage fields of this magnitude are required. Photographs, diagrams and characteristic measurements are presented.

5. A Balanced Receiving Circuit for Kennelly-Heaviside Layer Observations. HARRY R. MIMNO AND P. H. WANG, *Cruft Laboratory, Harvard University.*—In experiments on the effective height of the Kennelly-Heaviside layers, it is frequently desirable to place the receiving set near the transmitting apparatus. Unless precautions are taken, the direct radiation from the transmitting antenna will paralyze any receiving set which is sensitive enough to detect weak echoes. In previous experiments it has been customary to design the receiver so that it would recover as rapidly as possible from an overload. The resulting "stiffness" of the receiver has determined the resolving power of the apparatus. However, in a permanent laboratory installation it seems more logical to construct the transmitter and receiver as a duplex radiofrequency network which can respond to the reflected wave without any interference from the direct radiation. There are two convenient methods. The transmitting-set modulator may be used to vary the receiving-set gain, or the radiofrequency voltage induced in the receiving antenna may be balanced by an equal and opposite voltage obtained directly from the transmitter coils. By using the second method, successful results have been obtained with the receiving apparatus about four meters from the transmitter. Several types of receiving antennas have been employed directly under the transmitting antenna.

6. The Reflecting Layers of the Upper Atmosphere. R. C. COLWELL AND I. O. MYERS, *West Virginia University.*—During recent years it has been shown by Appleton (and others) that there are two ionized layers in

the upper atmosphere, one of which the lower (*E* layer) reflects waves above 100 meters, but is penetrated by shorter waves. The shorter waves are reflected from the upper (or *F*) layer. During the past autumn simultaneous observations were made upon the short wave from station W8XK (6140 kc) and the long wave from KDKA (980 kc). Both stations are located at Saxonburg, Pa. The fading curves obtained were plotted upon maps of the United States Department of Agriculture Weather Bureau. It is seen at once that the signal strength of the long waves varies after nightfall according to the change in barometric pressure. While the short waves have the same characteristic curve regardless of the weather. This indicates that the *E* layer is in the region connected with the varying pressures while the *F* layer is unaffected. The *F* (Appleton) layer covers the sky in a more or less uniform sheet, while the *E* (Kennelly-Heaviside) layer is concentrated in the regions of low pressure and is most active in the eastern half of the cyclone.

7. Absorption and Scattering of Neutrons. J. R. DUNNING AND G. B. PEGRAM, *Columbia University.*—The source of neutrons was beryllium powder in a glass bulb containing radon. The neutrons emitted from the beryllium under the alpha-particle bombardment were detected through the sudden ionizations produced by single recoil atoms in the ionization chamber of a vaccum tube detection apparatus that responds linearly to sudden increases of current but is little affected by the large but comparatively steady ionization caused by gamma-rays (see abstract December, 1932, meeting). With 400 millicuries of radon in the source 30 cm from the ionization chamber, about 20 neutrons per minute were recorded. Gross absorption curves were taken for lead, paraffin, water and aluminum. Paraffin and water show an absorption of the same order of magnitude as lead, per cm thickness. An absorbing cylinder of lead 20 cm long, 2.5 cm diameter cuts down to one-sixth the number of neutrons recorded, but there is evidence that some of the residual neutrons are neutrons scattered by surrounding objects. A large scattering by water is shown when, with a lead cylinder between source and ionization chamber, water is placed alongside the cylinder. The number of neutrons scattered into the chamber by the water is then nearly equal to the number in the direct unshielded beam. Scattering from lead has also been observed.

8. Detection of the Ionization by Individual Cosmic Rays. W. F. G. SWANN, *Bartol Research Foundation of the Franklin Institute.*—A copper cylinder 15 cm long and 7.5 cm in diameter was filled to 4 atmospheres with argon. It was supplied with a collecting electrode connected to a F. P. 54 General Electric Pliotron, which operated an amplifier designed to record upon moving photographic paper, through the medium of a galvanometer of period 0.1 second. A potential of 1000 volts was applied to the copper cylinder through a filter, and the sensitivity and resolving time of the instrument was sufficient to bring out the records of the individual cosmic rays or groups. Two such systems were used, and were arranged so that the axes of the copper cylinders were vertical, and in line. The simultaneous occurrence of records of a cosmic ray by the two instruments was a guarantee that in those cases the effect was produced by a ray which had passed through both cylinders and was not due to an ordinary beta-particle. Those simultaneous kicks which were equal and which also had the maximum values represented rays, or groups, which had passed the full length of both cylinders. They afforded a means of determining the ionization per centimeter of path of the ray or group, which, subject to certain corrections to be provided for in a modified form of apparatus, and arising from the time of collection of the ions came out as about 200 ions per centimeter of path per atmosphere at 4 atmospheres.

9. The Angular Distribution of the Low Energy Cosmic Rays. THOMAS H. JOHNSON AND E. C. STEVENSON, *Bartol Research Foundation, Swarthmore, Pa.*—With three Geiger-Mueller counters as a telescope the angular distribution of the cosmic radiation has been measured both with and without a lead absorbing block (3.7 cm thick) inserted just above the lowest counter. The cross-sectional area of the lead was the same as that of the sensitive volumes of the counters so that scattering effects were, as far as possible, eliminated. The intensity of soft rays from any direction is given by the difference in counting rates with and without the lead and the angular distribution of these is at least as concentrated about the vertical direction as that of the rays which are not absorbed by the lead. If the absorbed rays are regarded as secondaries produced by the penetrating rays the results show that the secondary ray has the same direction as its primary ray. The experiments are being continued with other thicknesses of lead.

10. The Response of Barrier-Layer Photo-Cells to X-Rays. PAUL R. GLEASON, *Colgate University.*—A number of Weston Photronic cells and Tungsram Type S_1 cells have been compared under exposure to the general radiation of x-ray tubes operated up to 200 kv. Special attention had to be given to the shielding of the cells and connections as electrostatic surges easily break down the contacts at the thin metallic electrode. The response of a single cell is not proportional to that of a standard ionization chamber exposed to the same radiation. In the region studied, the cells seem most sensitive at about 0.22A effective wave-length, falling off nearly 40 percent at the shortest wave-lengths. A combination of two cells with suitable filters was in agreement with the standard ionization chamber to within 10 percent until effective wave-length 0.17A was reached, failing by about 25 percent at shorter wave-lengths. The photronic cells average 1.2 microamperes when x-rays are incident of one roentgen per second. Two cells having equal sensitivities to light do not necessarily show the same response to x-rays. At a given temperature, the voltage-current characteristic curve is independent of whether light or x-rays are exciting it. The lag in response to x-rays is quite significant, particularly with the more penetrating rays. Some 15 seconds are required on the

average as compared with six seconds for the same deflection with the same galvanometer under exposure to light.

11. Variation of Photoelectric Efficiency with Work Function in the Extreme Ultraviolet. CARL KENTY, *General Electric Vapor Lamp Company, Hoboken, N. J.*—The following table shows the relative magnitudes (for each gas) of the approximate saturation currents obtained from a W surface treated in various ways when exposed to the full radiation from a 100 m.a. positive column discharge in He, Ne, or A at 0.5 mm pressure. Evidence that currents similar to these are mainly caused by the photoelectric

Surface	Work Function (volts)	He	Ne	A
W−O	>6.7	100	100	90
W	4.9	78	68	100
Mg(*A*)	3.7	39	12	60
Mg(*B*)	<3.0	22		

action of the resonance radiations concerned have already been reported (C. Kenty, Phys. Rev. **43**, 18 (1933) and **38**, 377L (1931)). In the table W−O refers to oxidized tungsten, W, to tungsten degassed by heating repeatedly in vacuum to 2000°K, Mg(*A*) to an evaporated Mg layer slightly contaminated with gas and Mg(*B*) to a relatively clean Mg surface. The work functions were located approximately in each case by the method of filters with a quartz Hg lamp as source. Regarding the actual magnitudes of the photoelectric efficiencies concerned, values of 1–5 electrons per 100 quanta, depending on the gas and cleanliness of the surface (Ni) have already been reported (C. Kenty, Phys. Rev. **38**, 2079L (1931)); these measurements are being extended to W and other surfaces.

12. Action of Mercury Metastable Atoms on Metal Surfaces. S. SONKIN AND HAROLD W. WEBB, *Columbia University.*—Mercury atoms were excited to the 2^3P_0 metastable state by electron impact, and the electron emission produced by these atoms when they struck the metal surfaces under test was measured. When the experimental tube and electrodes were thoroughly baked and outgassed different metals were found to give very nearly the same response to mercury metastable atoms. The sensitivity of any surface that was thoroughly outgassed was found to have a stable value to which it invariably returned after temporary changes which followed heating of the surface. Detailed investigation of such changes in response for a tungsten surface, with different mercury vapor pressures, showed that the presence of mercury atoms was essential for the formation of the sensitive surface and that this surface probably consisted of a layer of mercury atoms. There is evidence also that oxygen atoms play an important part in the formation of this surface and together with the mercury atoms form a complex but stable arrangement giving a very constant sensitivity to mercury metastable atoms. Under certain critical conditions very large transient values of sensitivity were observed. No correlation between the sensitivity to metastable atoms and the photoelectric response was found.

13. Dissociation Products of Carbon Monoxide Formed by Primary Electron Impact. W. WALLACE LOZIER, *National Research Fellow, Princeton University.*—The atomic ions produced by electrons passing through carbon monoxide at low pressures have been studied in an experimental tube similar to that described by Tate and Lozier (Phys. Rev. **39**, 254 (1932)). This new apparatus was constructed of tantalum, tungsten, and glass. The experimental pressure of CO used was 3×10^{-5} mm Hg and the electron current was 10^{-7} amp. O^- and C^+ ions both appear as primary products of electron impact. The O^- ions first appear at an electron energy of 9.5 ± 0.1 volts electron energy. Their ionization current when plotted against electron energy yields a sharp peak 1.2 volts wide at half-maximum. At 20.9 ± 0.1 volts electron energy O^- ions again appear, accompanied by equal numbers of C^+ ions. At 22.8 ± 0.1 volts electron energy the production of C^+ ions increases very markedly; this increase is unaccompanied by a like one in the production of negative ions. The ions mentioned above possess kinetic energies ranging from zero up to several volts. Interpretations of these results will be attempted.

14. Ionization of Argon, Neon and Helium by A, Ne and He Atoms. CHARLES J. BRASEFIELD, *Yale University.*—The ionization of argon, neon and helium under impact of A, Ne and He atoms was investigated by a method which eliminated errors due to secondary electrons. When argon, neon and helium were bombarded with their own atoms, ionization was found to set in at approximately 100 equivalent volts in each case. When either of these three rare gases was bombarded with atoms of the other two, no ionization could be detected, at least below 150 equivalent volts.

15. Magnetic Focussing Method for the Angular Distribution of Electrons after Elastic and Inelastic Collisions with Gases. A. P. GAGGE, *Yale University.* (*Introduced by John Zeleny.*)—A new method is described for studying the angular distribution of electrons after elastic and inelastic collisions in gases. The whole apparatus is placed in a uniform magnetic field. The primary electron beam is accelerated from a heated filament to a coaxial cylinder and passes through two slits into the scattering region. The filament, slits, and scattering region all lie on a circle, which may be rotated about an axis through the scattering region. The scattered electrons are focussed, as in a β-ray spectroscope, and enter the narrow opening of a movable Faraday collector. The fixed slit subtends a small angle at the scattering region and so defines the scattered direction. The various velocities of the scattered electrons are selected by moving the collector along the locus of foci. This arrangement has two advantages over the previous methods for angular distribution study. Since all electronic paths are circular, the angular distribution may be

studied completely to 180°. Secondly, since the collected beams are limited by only one slit and are magnetically focussed, the intensity of the collected beam is more efficiently preserved. For this reason the method is especially suitable for studying the elastic and inelastic collisions of slow electrons. Distribution curves for mercury vapor are shown.

16. Small-Angle Inelastic Scattering of Electrons in Helium, Mercury and Hydrogen. S. N. VAN VOORHIS, *Princeton University.* (*Introduced by G. P. Harnwell.*)—The variation of inelastic scattering with angle has been measured for electrons of from 100 to 300 volts energy, and for angles of from 0° to about 15° scattering. In helium the 21.1 volt loss ($1^1S_0-2^1P_1$) was used; in mercury, the 6.7 volt loss, and in hydrogen, a most probable loss of 12.6 volts was used. An electrostatic analyzer separated those electrons which had suffered energy loss, permitting readings to be taken without disturbance by the large number of unscattered electrons. A decided decrease in scattering at very small angles is found in all three cases, the maximum scattering *per unit solid angle* occurring at angles of from 2° to 6° depending on the energy of the electrons and the scattering substance. It is also found that all scattering curves for one gas are superposable if plotted against the product of the energy of the electrons and the angle of scattering, as abscissa. The data cannot be fitted nearly as well by use of the quantity $(k_0^2+k_1^2-2k_0k_1\cos\theta)^{\frac{1}{2}}$ given by the simple Born theory as abscissa.

17. The Diffraction of Electrons by Single Molecules. LOUIS R. MAXWELL, M. E. JEFFERSON AND V. M. MOSLEY, *Bureau of Chemistry and Soils, Washington, D. C.*—Diffraction photographs have been obtained for electrons (20–40 kv) scattered by the vapors of carbon tetrachloride (CCl_4), iodine (I_2), and 1,4-diiodobenzene ($C_6H_4I_2$). The following results have been interpreted by the use of the Debye scattering formula developed for coherent scattering of x-rays from polyatomic gases, together with the application of the theory of Mott and Bethe for elastic electron scattering by monatomic gases: (1) Carbon tetrachloride; the first three diffraction rings were measured and the corresponding values of $(1/\lambda)\sin\frac{1}{2}\theta$ were found to be 0.197, 0.364, and 0.548, corresponding to 2.98A as the Cl−Cl distance. These results are in good agreement with previous electron diffraction data obtained by R. Wierl (Ann. d. Physik **8**, 521 (1931)). (2) Iodine; for this molecule the I−I separation was found to be 2.64A, in agreement with 2.66A computed from band spectra data (W. G. Brown, Rev. Mod. Phys. **4**, 83 (1932) by Mulliken), and also with 2.70A the distance obtained from the structure analysis of crystalline iodine by x-ray diffraction. (P. M. Harris, E. Mack, Jr., and F. C. Blake, J.A.C.S. **50**, 1583 (1928); (3) 1,4-diiodobenzene; the computed scattering formula predicts the appearance of a maximum at about $(1/\lambda)\sin\frac{1}{2}\theta=0.22$. This diffraction ring was very prominent on the photographic plates and was used primarily for determining the I−I separation. The distance obtained was 6.85A±0.10. From an x-ray determination of the crystalline structure S. B. Hendricks has also obtained 6.85±0.10 for the I−I distance. In this case as well as for iodine it is seen that the intermolecular distances are the same in the solid and vapor phases.

18. Diffraction of Electrons by Metal Surfaces. L. H. GERMER, *Bell Telephone Laboratories, New York City.*—Fast electrons are scattered from a metal surface ruled with parallel scratches. An excellent diffraction pattern is produced (characteristic of the metal) when the scratches lie normal to the plane of incidence of the electrons. Only an extremely weak pattern is obtained with the scratches parallel to the plane of incidence. This experiment confirms directly the theory of G. P. Thomson that the diffraction of electrons from a massive polycrystalline surface results from the transmission of the electrons through little mounds of material projecting from the surface. It does not, however, confirm his view that the failure of polished surfaces to give diffraction patterns is due to the existence of a surface layer of amorphous metal. Further evidence against the amorphous layer theory has been obtained by scattering electrons from the surfaces of drawn wires. A wire drawn through a good die gives no diffraction pattern. Wires drawn through a broken die have minute fins projecting from their surfaces, caused by the forcing of metal into the cracks of the die. Such wires sometimes give complete diffraction patterns extending into the shadow of the wire. These must certainly be produced by transmission through severely worked material which is still crystalline.

19. Electron Optics. C. J. DAVISSON, *Bell Telephone Laboratories, Inc.*—The term "electron optics" is used to designate the theory and practice of focussing beams of electrons by electric and magnetic fields. Interest in this subject—by no means a new one—has increased greatly during the last few years. In 1926 Brusch showed by calculation and demonstrated by experiment that the field of a short circular coil magnet has for electrons of a given speed the properties of a positive lens of definite and calculable focal length. The possibilities of electron optical systems in which this type of lens is employed have been explored recently by Ruska and Knoll. Sharply defined images of stencils have been produced and magnifications up to 400 times have been obtained. Images of emitting surfaces also have been formed by these experimenters. The magnetic lens systems is not so well adapted to projection of this kind, however, as the purely electrical system. In this the "lenses" are the distorted fields about apertures in charged electrodes. Brüche and Johannson have demonstrated the important possibilities of this type of system in portraying the "brightness" patterns of emitting surfaces. Our interest in this subject in the Bell Telephone Laboratories has been primarily in the production of beams of electrons of prescribed characteristics—in improvement of the so-called "electron gun" as a collimator. A theory of electron optical systems of the electrical type has been developed. Its usefulness for purposes of electron optical design has been demonstrated in numerous tests. (Invited paper.)

20. Diffraction of Low-Speed Electrons. H. E. FARNSWORTH, *Brown University.*—Experiments with low-speed electrons have shown many deviations from the results to be expected on the basis of de Broglie's original relation. These deviations exist for normal incidence as well as for glancing angles of incidence used in the Bragg method, and may appear as a secondary or fine structure of the main diffraction beams. The relative intensities of the various components are extremely sensitive to small changes in the angle of incidence. This results in large variations of the relative integrated intensities of the main diffraction beams with small changes in angle of incidence. It thus appears that an understanding of the phenomenon should contain information on still obscure points in the present view of the solid state, such as the concept of an average inner potential, deviations from such an average value, and interaction between electrons in crystals. The following further experiments have been undertaken to determine possible surface effects, and in particular the "surface action" considered by v. Laue. (1) A study of the characteristics of a thin film of one metal deposited by evaporation on a single crystal of another metal. (2) Investigation of reflection from opposite sides of a given set of atomic planes when using primary electrons which enter different faces of the same crystal in the two cases. The first experiment shows that the fine structure characteristics for the film are essentially the same as those for a massive crystal of the same metal, and thus eliminates surface irregularities as a possible cause of fine structure differences. The second experiment indicates that there is an unsymmetrical reflection from opposite sides of an atomic plane, and appears to have a significant bearing on the interpretation of the fine structure. (Invited paper.)

21. A Lens for Cosmic-Ray Electrons. W. F. G. SWANN AND W. E. DANFORTH, JR., *Bartol Research Foundation of the Franklin Institute.*—The design involves the use of two vertical concentric tubes between which a potential difference is maintained. Along the axis of the tube two counters are placed, one above and the other below. It is then possible to focus the rays passing through one counter so as to pass through the other. The main features of the apparatus lie in the design of the tube. The fact that the field decreases with the distance from the axis, whereas in order to produce focussing it would have to increase, necessitates a compensation produced by causing the rays which are required to be bent through the greater angle to traverse a longer path than the others. The desired result is secured by flaring the ends of the tubes in such a manner that the different rays enter the field and also leave it at different points. The portions of the tube between the end flares have to be properly formed in order that the rays shall not be lost by passing through the walls. The characteristics may be described as follows. The tube system is one meter long. The distance between the two tubes is of the order of one centimeter, but varies along the length. The mean radius is five centimeters, at the entrance end. 10^8 volt-electrons passing through a point one meter above the upper end of the tubes would be focussed to a point one meter below the lower end, by a potential difference of 100,000 volts between the two cylinders. A ring counter is placed at the entrance end of the tubes, so that the rays which are recorded are those which pass through the ring counter and the conjugate foci. With the conditions cited, about five counts per day would be expected if all of the corpuscular rays had 10^8 volts velocity. A test of the two counters together with the circular counter in the absence of the cylinders should of course reveal a number of accidental counts sufficiently small to avoid masking the main effect. A preliminary test has indicated only one count in thirty-six hours with this arrangement. If the linear dimensions of the apparatus be increased certain advantages are gained. The field necessary to produce focussing of rays of assigned energy diminishes inversely in proportion to the linear dimensions, so that with an apparatus extending over a length of thirty meters, a field strength of 15,000 volts per centimeter may be utilized and the apparatus can be used in air. The principal advantage, however, is gained in an increase in the number of rays which can be obtained. Increase of the linear dimension in a constant ratio does not increase the solid angle but it does increase the area permissible for the initial counter. With a system thirty meters long, the counts can be increased to such an extent as will permit 500 counts per day and provide a source of radiation of convenient strength for use in experiments. By increasing the maximum field between the tubes to 20,000 volts per centimeter, which is permissible, the distance between the counters may be shortened to about 20 meters, which is a distance attainable without very much difficulty. This would increase the number of counts. (Invited paper.)

22. On Electron Beams in High Vacuum. VLADIMIR K. ZWORYKIN, *Research Division, RCA Victor Company, Camden, N. J.*—In order to concentrate a beam of electrons into a high intensity, sharply defined bundle, various methods have been used. The concentration of electron beams in high vacuum depends entirely upon fields of force, either electric or magnetic, while in low vacuum or in rarefied rare gas it depends also upon the action of gas molecules. In high vacuum the fields of force act upon the electron beam similar to the action of lenses upon a beam of light. An improperly shaped field produces effects similar to spherical aberration in poorly corrected lenses; non-uniform velocity of electrons in the beam results in effects similar to chromatic aberration of light. This optical analogy is not perfect. In the case of the electron beam the velocity varies continuously throughout most of the path and indices of refraction employed usually are greater than in the optical case. Moreover, space charge in beams of high intensity limits the concentration attainable: consequently, even theoretically, an electron beam can never be brought to a mathematical point as in the case of light optics. Other secondary effects are described. In focussing electron beams, both electrostatic and electromagnetic methods have been used extensively. The electrostatic method, however, seems to be preferable, especially when the beam is to be deflected. Precautions should be taken not to destroy the focussing of the beam during deflection. A

list of references on the subject is given at the end of the paper. (Invited paper.)

23. The Decomposition of Ozone. ARTHUR W. EWELL, *Worcester Polytechnic Institute.*—Warburg and later Clement studied the decomposition of ozone in the absence of oxidizable material, water vapor and catalytic agents. They found the reaction to be $2O_3 = 3O_2$ or bimolecular and that the velocity constant at 16°C was of the order of 10^{-10}, the concentration being expressed in parts per million by volume and the time in minutes—thus making ozone relatively stable under these conditions. The writer has studied the decomposition of ozone under the various conditions of its extensive use in purifying air in cold storage plants, air conditioning, etc. Under these practical conditions the reaction is monomolecular, $O_3 = O_2 + O$, and very closely follows the equation $dc/dt = -kc$. The value of k varies from 0.01 to 0.1, corresponding to half disappearance in from 69 to 6.9 minutes. Experimental observations of the concentration, c, at different times, t, confirm the two equations $c = C(1 - e^{-kt})$ and $c = Ce^{-kt'}$ where C is the final equilibrium concentration, t the time after the supply $m = kC$ per minute starts, and t' the time after the supply of ozone is cut off.

24. A Logarithmic Protractor. H. J. YEARIAN, *Purdue University.*—An instrument has been designed to rapidly transpose microphotometer records to blackening, according to the relation: $S = \log(i_0/i) = \log(d_0/d)$ where i_0 is the incident and i the transmitted intensity, d_0 and d the corresponding photometer deflections. To a vertical axle mounted on a parallel ruler, is fixed a drum and a brass template cut according to the curve $\log \rho = a\theta$. A cable passing around the drum moves a plotting pencil along the ruler as the template and drum are turned. A zero line is placed parallel to the ruler and passing through the axis of drum and template. In use, as the axis of the instrument is run along the zero line of the record to be transposed, the template is turned to keep its edge in coincidence with the record and the zero line of the instrument. The pencil then plots the logarithm of the microphotometer deflection, and the distance between the plotted curve and the plotted position of d_0 is a measure of the blackening. The instrument has been found exceedingly useful and could be adapted to transposition according to almost any single valued function of the type $f(\rho) = a\theta$, within reasonable limits of ρ and θ.

25. A Note on Photographic Intensity Measurement in the Schumann Region. EDWIN G. SCHNEIDER, *Harvard University.*—The object of the experiment was to measure the transmission of a piece of optical fluorite for a series of wave-lengths between 1250 and 1600A by a photographic method. The light from a direct-current hydrogen discharge entered a vacuum spectrograph and was recorded on a Cramer Contrast plate sensitized with a ten percent solution of Cenco Pump Oil 11021-C in petroleum ether. It was necessary to assume the reciprocity relation to deduce the transmission from the relative times of exposure. This assumption is held to be valid in view of the work of G. R. Harrison (J. Opt. Soc. Am. **11**, 341 and **20**, 313) for the plate and oil chosen. The greatest source of random error was probably the irregularity of the plate grain. Ten determinations of each point on the wave-length transmission curve were made; the error of location of each point is of the order of magnitude of three percent. The results agree with those obtained by W. M. Powell photoelectrically within the limit of error. The same piece of fluorite was used in comparing the two methods of measurement.

26. Intensity Measurements Between 1650A and 1240A with a Photoelectric Cell. W. M. POWELL, *Harvard University.*—The source is a hydrogen discharge tube with a 3 mm water-cooled quartz capillary fed by 800 volts and 1 ampere d.c. A vacuum grating spectrograph is used as a monochromator to shine light into a photographic cell with a fluorite window. The grating, of 1 meter radius and 15,000 lines to the inch, can be turned and the slit in front of the cell can be focussed from outside. The photoelectric surface is platinum. The cell contains argon at 7 mm pressure. Voltages from 250 to 450 are used for varying the sensitivity. Currents from 10^{-9} to 10^{-10} amperes with slit widths of 0.05 mm are measured by a Compton electrometer, and a 3×10^{-10} ohms resistance to ground. The absorption of pieces of fluorite of different thicknesses have been measured. It appears that the surfaces are very sensitive to polishing. Chemically precipitated fluorite powder and water on silk on a piece of glass produces the best results so far. The accuracy of measurement is of the order of 1.5%. The resolving power is about 1.5 Angstroms.

27. Improvements in the Mechanical Interval Sorter for Complex Spectra. GEORGE R. HARRISON, *Massachusetts Institute of Technology.* The spectrum interval sorter recently described (R.S.I. **3**, 753 (1932)) has been improved so that greater wave-number separations can be recorded without increased error due to irregular tape stretch. 35 mm paper tape with perforated edges is used with a sprocket wheel device which prevents transmission of forces along the tape beyond the one meter lengths which are being recorded. By the use of formulas for the probability of any number of accidental coincidences, and by analysis of a number of different types of complex spectra which have already been worked out, one can arrive at a set of optimum conditions for making apparent the atomic energy levels by application of the combination principle. In most cases it is best to divide the spectrum up into groups of lines according to intensity or some other characteristic and to compare the records obtained with the various groups, rather than to use all the lines at once. The machine is now being used in the analysis of certain rare earths and complex hot spark spectra.

28. Transmission Band of Alkali Metals in Ultraviolet. R. W. WOOD, *Johns Hopkins University.*—The high transparency of sodium and potassium films deposited on the inner surface of quartz bulbs at liquid air temperatures was described by the author in 1919 (Phil. Mag.). The matter has now been more fully investigated. Lithium is highly

transparent in the region below 1800A, sodium at 1900A, potassium at 2800A, rubidium at 3100A and caesium at 4300A. A film of the latter metal transmits a blue color as pure as that exhibited by dense cobalt glass or a strong solution of cuprammonium. A technique has been developed of making durable films for use as ray filters, and quantitative measurements of the transmission in various spectral regions have been made.

29. Internal Resonance in the CO Molecule. G. H. DIEKE, *The Johns Hopkins University.*—The initial state ($^3\Sigma$) of the third positive CO bands shows some perturbations of very remarkable characteristics. The deviations from the simple quadratic formula show for the ten observed perturbations the characteristic form of resonance curves. The energies show, however, a constant displacement of roughly 25 cm^{-1} after each perturbation. Such behavior must be expected if the nondiagonal elements in the perturbation matrix of two levels is proportional to J. As all three triplet components are affected in the same way the perturbing term must be also a $^3\Sigma$-level. The only known term of the CO molecule which satisfies all the requirements is the initial $^3\Sigma$-state of the far red bands. The successive perturbations are then caused by successive high vibrational states of this level, which must have a much larger moment of inertia. The perturbations are larger than those usually found. The deviations in a single perturbation exceed 50 cm^{-1} and the cumulative effect of all ten perturbations is about 200 cm^{-1}. The intensities of the strongly perturbed lines are abnormally weak in all branches.

30. The Effect of Hyperfine Structure on Magnetic Depolarization of Resonance Radiation. ALLAN C. G. MITCHELL, *New York University.*—Breit [Rev. Modern Physics, (in press)] has derived formulae giving the polarization $P(H)$ and the angle of maximum polarization φ of a resonance line showing hyperfine structure, as a function of a weak magnetic field applied in the direction of observation of the resonance radiation. The formulae give a means of estimating the effect of hyperfine structure on the calculation of the mean life τ of an excited atom from experiments on the magnetic depolarization and rotation of the plane of polarization of resonance radiation. The calculation has been carried through for the case of the resonance line of Cd (λ 3261) and that of Hg (λ 2537), and it is found that the differences between the value of τ calculated using hyperfine structure data and that calculated from $\tan 2\varphi$ by the usual non-hyperfine structure method lie well within the experimental error. $P(H)/P_0$ is found to be practically the same taking into account or neglecting hyperfine structure. This is due to the fact that the greatest contribution to the polarization in these cases comes from the isotopes having no nuclear spin and the g-value for the upper state of these isotopes is larger than any other upper hyperfine structure state involved. The mean lives of the visible triplet in mercury are also discussed.

31. Zeeman Effect for Perturbed N_2^+ Terms. ALLAN E. PARKER, *Yale University.*—A study of the Zeeman effect for the N_2^+ bands has been made with plates taken at six different field strengths from 6000 to 27,000 gauss. The unperturbed bands show no Zeeman effect as is to be expected for a $^2\Sigma \rightarrow {}^2\Sigma$ transition having no appreciable spin-doubling. Zeeman patterns for the perturbed 1, 3 and 3, 5 bands are observed. The perturbation in the T_1' terms of the 1, 3 band reaches a maximum at $K'=13$ but does not vanish at higher K' values. Zeeman patterns were calculated from Hill's formula for $^2\Sigma$ states assuming as ν_0, the separations between the T_1 (perturbed) and T_2 (unperturbed) terms. Excellent agreement was found between the observed and computed patterns for $K'>14$. This is notable as the T_2' terms in the absence of the field show no perturbation and would be expected to show no change as a result of the magnetic field. Furthermore the T_2' terms for the K' values corresponding to the largest perturbation of the T_1' terms, give rise to doublets in the field as do the T_1' terms. Similar results are obtained for the 3, 5 band. A consideration of the interactions with the perturbing $^2\Pi$ state gives an explanation of these patterns.

32. Conservation Theorems in Quantum Mechanics. E. L. HILL, *University of Minnesota.*—The perturbation theory is generally developed from the energy equation alone. It is well known that this is but one of a set of quantization equations equal in number to the number of degrees of freedom of the system. If the perturbation function commutes with one or more of the corresponding auxiliary operators, the perturbation equations are separable into two or more unrelated groups implying conservation theorems for the associated dynamical variables. The general theory is easily written out. Application has been made to the theory of electron scattering by a given field of force in order to exhibit explicitly the conservation of angular momentum. This leads to a scattering formula expressed as a Fourier sum with the associated Legendre polynomials as basic functions.

33. Symmetry Properties and the Indistinguishability of Similar Particles. E. E. WITMER AND J. P. VINTI, *University of Pennsylvania.*—It has been shown by Heisenberg and Wigner that in a system of n similar particles, the wave functions fall into a number of non-combining sets with different symmetry properties. Of these it has been found empirically that for a given type of particle only those states occur whose wave functions are symmetrical in all the like particles or else antisymmetrical in all the like particles. The authors show that this result follows from the principle of the indistinguishability of similar particles as applied to the probability density $\psi\bar{\psi}$, which requires that $\psi\bar{\psi}$, being in concept a measurable quantity, shall be invariant with respect to any interchange of like particles.

34. A Modification of Brillouin's Unified Statistics. R. B. LINDSAY, *Brown University.*—Brillouin has proposed the statistical assumption that the capacity of a cell in phase space depends on the number of particles in it. The capacity of a cell with p occupants is $1-pa$ where a is a parameter. According as $a=0$, -1 or $+1$, one gets the

classical, Bose or Fermi distribution law. The present paper investigates the case where a is not restricted but allowed to vary between 0 and $+1$, corresponding physically to a loosening of the Fermi restriction while still allowing less freedom of occupancy than the classical theory. The resulting distribution law is $N_i = n_i/(a+e^{-\alpha+E_i/kT})$, where N_i is the number of particles in the i-th energy shell containing n_i cells. In applying this law to a degenerate electron gas it is found that: (1) the zero-point energy now becomes $3/10 \cdot Nh^2/m \cdot (3aN/8\pi V)^{2/3}$ in place of the Fermi value $3/10 \cdot Nh^2/m \cdot (3N/8\pi V)^{2/3}$; (2) the contribution of the free electrons to the specific heat of a metal is still negligible even if a is as small as 1/10; (3) there is now a zero-point entropy proportional to $\log a$; (4) the thermal and electrical conductivity expressions are modified, but the Wiedemann-Franz law is still satisfied; (5) the Thomson thermoelectric coefficient for $0<a<1$ is larger than on the Fermi statistics, corresponding to better experimental agreement in several cases.

35. Field Electron Currents from Liquid Mercury Surfaces. J. W. BEAMS, *University of Virginia.*—Surge potentials of about 10^{-6} sec. duration (circuit time constant 4×10^{-6} sec.) were applied between a 2 cm steel spherical anode and a liquid mercury cathode in vacuo and the breakdown fields observed. The liquid mercury cathode was cooled to a few degrees above its freezing point and part of the tube was surrounded with dry ice to lower the vapor pressure of the mercury. The mercury surface of the cathode could be changed or cleaned by "overflowing" in vacuo. Since the free path of an electron was very great in comparison to the distance between the electrodes and the potential was applied for only about 10^{-6} sec. the discharge was initiated by electrons pulled out of the liquid mercury cathode (See Hull and Burger, Phys. Rev. **31**, 1121 (1928) and Snoddy, Phys. Rev. **37**, 1678 (1931) for analogous cases with solid metal electrodes). The short time of application of the electric field also prevented appreciable distortion of the mercury surface by the forces arising from the field. The electric field at the cathode necessary to produce sufficient field electron current to start the discharge, varied with the purity of the mercury and the condition of the surface. In the case of some of the mercury surfaces, fields of 9×10^5 volts per cm were required to start the discharge.

36. Electron Flow in Large Direct Currents. ERNST WEBER, *Polytechnic Institute of Brooklyn, Brooklyn, New York.*—It is shown experimentally that the distribution of large direct currents, subjected to a steady magnetic field perpendicular to the axis of flow, is not uniform over the cross section of the conductor. The macroscopic field theory of Maxwell must be altered to account for the non-uniform flow of electrons in direct currents, and it is shown that, for an adequate theory, Maxwell's picture of a non-compressible liquid must be changed into that of a compressible gas. The theory given presents, therefore, a combination of electron theory and macro-field theory for the conduction of electricity through metals. A comparison of the data obtained from experiments, still in progress, with theoretical results will then yield a first approximate determination of the number of free electrons in the metal. The effect investigated, although related to, is distinctly different from, the Hall effect.

37. Actinouranium and the Geologic Time Scale. FORREST WESTERN AND ARTHUR RUARK, *University of Pittsburgh.*—The actinium series arises from a uranium isotope U^{235}, or from two such isotopes, U^{235} and U^{239}, genetically connected. From work of Hahn-Meitner the first possibility is almost certainly right. Its consequences are studied. Equations are derived for finding the decay constant λ^4 of U^{235} (actinouranium) from data on radioactive minerals. They also yield the decay constant, λ_1, of U I, and the mineral age. Four minerals are studied, using two values of the "branching ratio." Means from Karlshus bröggerite and Wilberforce uraninite are:

Branching ratio B:	0.03	0.04
λ^4	2.28 10^{-9} yr.$^{-1}$	1.79 10^{-9} yr.$^{-1}$
λ_1	0.1514	0.1509

Ages (insensitive to B): Karlshus, 0.81 10^9 yr.; Wilberforce, 1.04 10^9 yr. The effect of leaching is analyzed. Very early leaching does not affect age determinations. Very recent leaching does not affect isotopic constitution of radiogenic lead. Equations for *uniform* leaching are developed and applied to Katanga pitchblende: Results $\lambda^4 = 2.83\ 10^9$ yr.$^{-1}$; age, 0.55 10^9 yr. Using our mean λ^4, "age" of the Vesuvian lava of Piutti-Migliacci is 1.5 10^9 yr., assuming that its lead is a mixture of RaG, AcD, ThD, and common Pb in the proportions occurring in average igneous rock.

38. Measurement of the Range of Alpha-Particles from Thorium with the Wilson Chamber. F. N. D. KURIE AND G. D. KNOPF, *Yale University.*—The range of the α-particles from thorium has been measured by the methods used by one of the authors previously (Rev. Sci. Inst. **3**, 655 (1932)). At 0°C and 760 mm the extrapolated number-distance range is 2.72 ± 0.03 cm. This range is derived from 300 tracks. It is pointed out that the great deviation of this range from that of Henderson and Nickerson (2.46 cm) is partially due to these authors' treatment of their data. The Geiger-Nuttall law is given according to the latest data for the uranium and thorium series in the form indicated by Gamow's theory.

39. The Unit Cell of Uranium Calculated from X-Ray Powder Method Data. THOMAS A. WILSON, *Union College, Schenectady.*—Photographs were supplied by Dr. W. P. Jesse, of the General Electric Research Laboratory which had been obtained by allowing unfiltered iron x-radiation to graze the surface of a block of uranium which had been rendered plane by filing in hydrogen. The uranium was of the highest purity obtainable. The block was rotated by hand in the x-ray camera. Exposure lasted $2\frac{3}{4}$ hours. The photographs showed 13 different plane reflections. By a mathematical analysis based on vectors, the equation for

the interplaner spacings of the parallelogram containing one uranium atom was found to be:

$$2.535^2/d^2 = h^2+k^2+l^2-0.878\,hk-0.758\,(h+k)l.$$

The unit cell of uranium accordingly has equal face perpendiculars of 2.535 Angstrom units in length, arranged in space at angles of 64°, 67° 45′, and 67° 45′ respectively. The volume of the cell is 20.26 cubic Angstrom units, which gives uranium an x-ray density of 19.32, as against 18.68 reported previously, a difference of 3.3 percent.

40. (a) **Raman Spectra Made with a Quartz High Potential Mercury Vacuum Tube (Hannovia Tube).** (b) **Exhibition of Phase-Reversal Zone-Plates Ruled on a Specially Constructed Machine.** R. W. Wood, *Johns Hopkins University.*

41. Related Figures on Circular Plates. R. C. Colwell, *West Virginia University.*—In 1850, Kirchhoff gave a complete mathematical solution for a vibrating circular plate with free edges. This solution in Bessel functions allows only for circles and diameters or combinations of these. When a plate is vibrated, however, many other figures are formed beside these mentioned above. A mathematical calculation shows that Kirchhoff's solution is complete but is for the simplest case only, corresponding to squares and rectangles on square plates. The proper combination of two Kirchhoff solutions will give the other figures. Photographic reproductions of certain families of curves will be shown.

42. Kowalewski's Top in Quantum Mechanics. Otto Laporte, *University of Michigan.*—It is well known that in classical mechanics algebraic integrals of the top equations only exist in the cases of Euler (asymmetric top, no electric moment), of Lagrange (symmetric top, electric moment parallel to the axis of figure) and of Kowalewski. The latter case is that of a symmetric top whose two equal moments of inertia are twice as large as the third ($A=B=2C$) with an electric moment perpendicular to the axis of figure. The quantum mechanical analogue to Euler's and Lagrange's cases being well known, Kowalewski's case was tried. If ϑ, φ, ψ are the Euler angles, $Q_I=Q_1+iQ_2$, $Q_{II}=Q_1-iQ_2$, linear combinations of the moment around the principal axes and

$$U=Q_I^2+4CFe\cdot\sin\vartheta\exp(i\psi),$$

then Kowalewski's integral becomes:

$$UU^*+U^*U+4h^2(Q_IQ_{II}+Q_{II}Q_I)=\text{const.},$$

which differs from the classical result by the symmetrization and by the last term proportional to h^2.

43. Non-unidirectional Emission of Hoffman's Stösse. W. F. G. Swann and C. G. Montgomery, *Bartol Research Foundation of the Franklin Institute.*—A piece of lead about 3″ thick and 30″ in diameter formed a central partition between the two halves of a large iron vessel 4′ high, containing nitrogen at 100 lbs. pressure. Two independent collecting electrode systems were provided for the top and bottom halves, so that the ionization in each could be independently measured. Each system was connected to an independent FP 54 pliotron system operating a short period galvanometer. The two galvanometers recorded simultaneously on a moving photographic record. Suitable means for compensation for average ionization current and for fluctuations of applied potential were employed. It was found that Stösse recorded themselves simultaneously in the two halves of the vessel, showing that the emission was not unidirectional. If the particles emitted were of electronic ionizing capacity, it would be necessary to suppose that at least 100 were emitted during each observation of Stösse. In order to provide further evidence, experiments were performed in which a counter system consisting of 3 sets of counters placed at different positions around the vessel were used, and arranged so as to discharge only if a ray went through each simultaneously. The probability that a ray would go through each of the counter sets with a total emission of 100 particles was less than unity, but in one out of two Stösse observed in this experiment a result was obtained indicating Stösse emission in each half accompanied by the record that the counters had simultaneously discharged.

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